

A modified reaction for the preparation of amidoalkyl naphthols using silica-supported Preyssler nano particles

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An improved green method for the synthesis of amidoalkyl naphthols through one-pot multi-component reaction of aryl aldehyde, β -naphthol and acetamide or acetonitrile (Ritter type reaction) in the presence of silica-supported Preyssler nano particles as effective catalyst is described.

Keywords: Silica-supported Preyssler nano particles; amidoalkyl naphthols; multi-component reactions

INTRODUCTION

One-pot multi-component reactions (MCRs) by virtue of their convergence, productivity, facile execution and high yield have attracted considerable attention in recent years [1]. There has been tremendous development in three or four component reactions, specially the Bignelli [2], Passerini [3], Ugi [4] and Mannich [5] reactions, which have further led to the renaissance of MCRs. Nevertheless, great efforts have been and still are being made to find new MCRs and improve the already known MCRs. One such reaction is the synthesis of amidoalkyl naphthols. These compounds are generally synthesized in a three-component reaction of aldehydes, urea or amide and β -naphthol in the presence of various catalysts such as montmorillonite K_{10} [6], $Ce(SO_4)_2$ [7], iodine [8], $K_5CoW_{12}O_{40} \cdot 3H_2O$ [9], p-TSA [10], $HClO_4 \cdot SiO_2$ [11], sulfamic acid [12] and silica-sulfuric acid [13]. Also, recently, Shaterian and co-workers have reported the synthesis of these compounds via a Ritter type reaction using one-pot MCR of aryl aldehydes, β -naphthol and acetonitrile in the presence of $FeCl_3 \cdot SiO_2$ as a catalyst [14].

The catalysts based on heteropolyacids have many advantages over liquid acid catalysts. They are not corrosive, environmentally benign, presenting fewer disposal problems. Solid heteropolyacids have attracted much attention in organic synthesis owing to easy work-up procedures, easy filtration, and minimization of

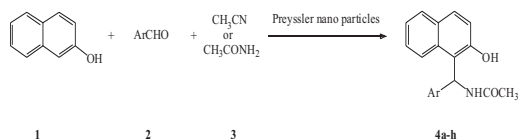
cost and waste generation due to reuse and recycling of the catalysts [15]. There have been many attempts to optimize these catalysts. Recently, Keggin nano catalysts have been synthesized [16]. In our attempt to use heteropolyacids as catalysts in organic reactions, we reported that Preyssler type heteropolyacids, $H_{14}[NaP_5W_{30}O_{110}]$, show strong catalytic action [17]. Due to the unique properties of nano particles along with their potential applications in different fields [18], we immobilized $H_{14}[NaP_5W_{30}O_{110}]$ into the SiO_2 nano particles [19] and investigated the catalytic behavior of this new catalyst.

Recently, we submitted a paper on the multi-component synthesis of amidoalkyl naphthols using Brønsted-acidic ionic liquids to the Synthetic Communication Journal. In continuation of our previous works on the applications of reusable acid catalysts in the synthesis of organic compounds [20–23] here we report an improved green method for the synthesis of amidoalkyl naphthols through one-pot multi-component reaction of aryl aldehyde, β -naphthol and acetamide under solvent-free conditions (Method A) or acetonitrile via a Ritter type reaction (Method B) in the presence of silica-supported Preyssler nano particles as a catalyst (Scheme 1).

RESULTS AND DISCUSSION

First, the three-component reaction of aryl aldehyde, β -naphthol, and acetamide was performed in the presence of silica-supported Preyssler nano particles as a catalyst under solvent-free conditions. In all cases, aromatic aldehydes

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Scheme 1

reacted successfully and gave the products in high yields. It was shown that aromatic aldehydes with electron-withdrawing groups reacted faster than those with electron-releasing groups, as expected (Table 1, Method A).

Next, the synthesis of amidoalkyl naphthols through a Ritter type reaction was investigated. Therefore, a mixture of aryl aldehyde, β -naphthol, and acetonitrile (both reactant and solvent) was heated under reflux in the presence of silica-supported Preyssler nano particles as a catalyst. In all cases, aromatic aldehydes with either electron-donating or electron-withdrawing groups gave the desired products via a Ritter type reaction (Table 1, Method B).

Table 1. Preyssler nano-particles catalyzed synthesis of amidoalkyl naphthols^a

Entry	Ar	Method		M.P. (°C)	
		A	B	Found	Reported
		time (min)/yield (%) ^b	time (h)/yield (%) ^b	(Method A)	
4a	C ₆ H ₅	5/95	8/87	241-242	242-243 [11]
4b	4-ClC ₆ H ₄	4/96	7/90	228-229	230-232 [11]
4c	4-FC ₆ H ₄	4/95	7/88	207-209	210-212 [11]
4d	4-MeC ₆ H ₄	7/88	8/87	220-222	222-223 [14]
4e	4-MeOC ₆ H ₄	8/84	8/86	184-185	183-185 [14]
4f	2-O ₂ NC ₆ H ₄	5/91	9/76	180-182	179-182 [14]
4g	3-O ₂ NC ₆ H ₄	4/93	7/91	213-215	212-214 [11]
4h	4-O ₂ NC ₆ H ₄	3/96	7/92	246-248	248-250 [14]

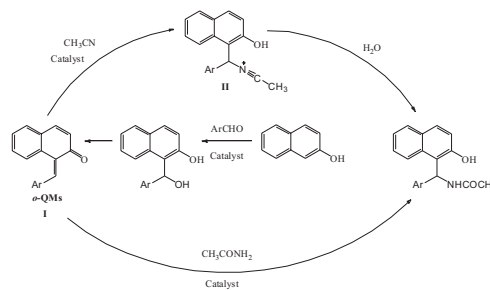
^aAll products were characterized by ¹HNMR and IR spectral data and comparison of their melting points with those of authentic samples.

^bIsolated yields

Although we did not investigate the reaction mechanism, based on the literature report [14], a plausible mechanism for these methods may be adopted, as depicted in scheme 2. As reported in the literature [8–10], the reaction of β -naphthol with aromatic aldehydes in the presence of an acid catalyst is known to give ortho-quinone methides (o-QMs) **I**. The same o-QMs generated *in situ* have reacted either with acetamide or with acetonitrile via intermediate **II** followed by hydrolysis in a Ritter type reaction to give the desired amidoalkyl naphthols.

In conclusion, we have reported herein a new efficient catalyst for the synthesis of amidoalkyl

naphthols through one-pot MCR of aryl aldehyde, β -naphthol and acetamide under solvent-free conditions (Method A) or acetonitrile via a Ritter type reaction (Method B) in the presence of silica-supported Preyssler nano particles as a catalyst. The catalyst can be reused after a simple work-up, a gradual decline of its activity being observed. High yields, shorter reaction times, simplicity of operation and easy work-up are some of the advantages of this protocol.



Scheme 2

EXPERIMENTAL

All compounds were known, and their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Melting points were recorded on an electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrophotometer in KBr disks. The ¹H NMR (500 MHz) spectra were recorded on a Bruker DRX500 spectrometer.

Preparation of amidoalkyl naphthols. General procedure.

Method A

A mixture of an aromatic aldehyde (1 mmol), β -naphthol (1 mmol), and acetamide (1.3 mmol) was heated at 90 °C in the presence of silica-supported Preyssler nano particles (0.03 mmol) for the indicated time (Table 1). After completion of the reaction, boiling ethanol was added to the reaction mixture. The catalyst was filtered off and the filtrate was then concentrated and cooled to room temperature. The precipitate was filtered off and recrystallized from aqueous ethanol to give pure amidoalkyl naphthols (Table 1).

Method B

A mixture of an aromatic aldehyde (1 mmol), β -naphthol (1 mmol) and acetonitrile (5 ml) (both reactant and solvent) was heated under reflux in the presence of silica-supported Preyssler nano

particles (0.03 mmol) for the indicated time (Table 1). The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was filtered off. The filtrate was then concentrated to afford a solid product, which was purified by re-crystallization from aqueous ethanol (Table 1).

Table 2. Comparison of the efficiency of Preyssler nano particles (fresh and reused) in the synthesis of amidoalkyl naphthols by method A

Entry	Ar	Yield ^a , %		
		First use	Second use	Third use
1	C ₆ H ₅	95	93	92
2	4-ClC ₆ H ₄	96	93	91
3	4-MeC ₆ H ₄	88	87	85

^aIsolated yields

Selected ¹H NMR & IR data

Compound 4a: ¹H NMR (500 MHz, DMSO-d₆, δppm): 1.98 (s, 3H, CH₃), 7.10–7.40 (m, 9H), 7.76 (d, 1H, *J* = 8.8 Hz), 7.80 (d, 1H, *J* = 8.0 Hz), 7.84 (br., 1H, NH), 8.43 (d, 1H, *J* = 8.3 Hz), 9.98 (s, 1H, OH); IR (KBr disc): ν 3400 (NH), 3246 (OH), 1640 cm⁻¹ (C=O).

Compound 4b: ¹H NMR (500 MHz, DMSO-d₆, δppm): 1.98 (s, 3H, CH₃), 7.09 (d, 1H, *J* = 8.1 Hz), 7.15 (d, 2H, *J* = 8.3 Hz), 7.21 (d, 1H, *J* = 8.8 Hz), 7.27 (t, 1H, *J* = 7.3 Hz), 7.30 (d, 2H, *J* = 8.5 Hz), 7.38 (t, 1H, *J* = 7.3 Hz), 7.75–7.85 (m, 3H), 8.46 (d, 1H, *J* = 8.1 Hz), 10.03 (s br., 1H, OH); IR (KBr disc): ν 3392 (NH), 3065 (OH), 1638 cm⁻¹ (C=O).

Compound 4g: ¹H NMR (500 MHz, DMSO-d₆, δppm): 2.02 (s, 3H, CH₃), 7.18 (d, 1H, *J* = 8.0 Hz), 7.22 (d, 1H, *J* = 8.8 Hz), 7.29 (t, 1H, *J* = 7.3 Hz), 7.41 (t, 1H, *J* = 7.4 Hz), 7.50–7.60 (m, 2H), 7.80–7.85 (m, 2H), 7.86 (br, 1H, NH), 8.01 (s, 1H), 8.03–8.07 (m, 1H), 8.61 (d, 1H, *J* = 8.0 Hz), 10.12 (s, 1H, OH); IR (KBr disc): ν 3375 (NH), 3223 (OH), 1648 (CO), 1524 & 1350 cm⁻¹ (NO₂).

Compound 4h: ¹H NMR (500 MHz, DMSO-d₆, δppm): 2.02 (s, 3H, CH₃), 7.18 (d, 1H, *J* = 7.8 Hz), 7.22 (d, 1H, *J* = 8.8 Hz), 7.28 (t, 1H, *J* = 7.3 Hz), 7.35–7.45 (m, 3H), 7.82 (t, 3H, *J* = 9.3 Hz), 8.13 (d, 2H, *J* = 8.6 Hz), 8.57 (d, 1H, *J* = 7.8 Hz), 10.11 (s, 1H, OH); IR (KBr disc): ν 3391 (NH), 3051 (OH), 1640 (C=O), 1523 & 1351 cm⁻¹ (NO₂).

Recycling of the catalyst

The catalyst recovered by filtration in method A was dried and reused for three times in reactions. The obtained results are summarized in Table 2. As it is shown, there is no significant loss of activity in using a recycled catalyst in this reaction.

REFERENCES

- (a) For special issue in MCRs, see *Tetrahedron*, **61**, 11299 (2005); (b) D. J. Ramon, M. Yus, *Angew. Chem., Int. Ed.*, **44**, 1602 (2005).
- (a) C. O. Kappe, *Eur. J. Med. Chem.*, **35**, 1043 (2000); (b) D. Dallinger, A. Stadler, C. O. Kappe, *Pure Appl. Chem.*, **76**, 1017 (2004).
- P. R. Krishna, G. Dayaker, P. V. Narasimha Reddy, *Tetrahedron Lett.*, **47**, 5977 (2006).
- (a) A. Domling, I. Ugi, *Angew. Chem., Int. Ed.*, **39**, 3168 (2000); (b) I. Ugi, B. Werner, A. Domling, *Molecules*, **8**, 53 (2003).
- M. Arend, B. Westermann, N. Risch, *Angew. Chem., Int. Ed.*, **37**, 1044 (1998).
- S. Kantevari, S. V. N. Vuppapalapati, L. Nagarapu, *Catal. Commun.*, **8**, 1857 (2007).
- N. P. Selvam, P. T. Perumal, *Tetrahedron Lett.*, **47**, 7481 (2006).
- B. Das, K. Laxminarayana, B. Ravikanth, B. R. Rao, *J. Mol. Catal. A: Chem.*, **261**, 180 (2007).
- L. Nagarapu, M. Baseeruddin, S. Apuri, S. Kantevari, *Catal. Commun.*, **8**, 1729 (2007).
- M. M. Khodaei, A. R. Khosropour, H. Moghanian, *Synlett*, 916 (2006).
- G. Mahdavinia, M. A. Bigdeli, M. M. Heravi, *Chin. Chem. Lett.*, **19**, 1171 (2008).
- S. B. Patil, P. R. Singh, M. P. Surpur, S. D. Samant, *Ultrason. Sonochem.*, **14**, 515 (2007).
- G. Srihari, M. Nagaraju, M. M. Murthy, *Helv. Chim. Acta*, **90**, 1497 (2007).
- H. R. Shaterian, H. Yarahmadi, *Tetrahedron Lett.*, **49**, 1297 (2008).
- M. M. Heravi, F. Derikvand, A. Haeri, H. A. Oskooie, F. F. Bamoharram, *Synth. Commun.*, **38**, 135 (2008).
- D. P. Sawant, A. Vinu, N. E. Jacob, F. Lefebvre, S. B. Halligudi, *J. Catal.*, **235**, (2005) 341.
- M. M. Heravi, S. Sajadi, H. A. Oskooie, R. Hekmat Shoar, F. F. Bamoharram, *Molecules*, **12**, 255 (2007).
- C. R. Gorla, N. W. Emanetoglu, S. Liang, W. E. Mago, Y. Lu, M. Wraback, H. Shen, *J. Appl. Phys.*, **85**, 2595 (1999).
- F. F. Bamoharram, M. M. Heravi, M. Roushani, M. R. Toosi, L. Jodeyr, *Green. Chem. Lett and Reviews.*, **2**, 35 (2009).
- M. M. Heravi, F. K. Behbahani, H. A. Oskooie, F. F. Bamoharram, *Chin. J. Chem.*, **25**, 2150 (2008).
- M. M. Heravi, Y. S. Beheshtiha, Z. Pirnia, S. Sadjadi, M. Adibi, *Syn. Commun.*, **39**, 3663 (2009).
- M. M. Heravi, F. K. Behbahani, Z. Daroogheha, H. A. Oskooie, *Russ. J. Org. Chem.*, **45**, 1108 (2009).
- M. M. Heravi, S. Sajadi, S. Sajadi, H. A. Oskooie, R. Hekmat Shoar, F. F. Bamoharram, *S. Afr. J. Chem.*, **62**, 1 (2009).

МОДИФИЦИРАНА РЕАКЦИЯ ЗА ПОЛУЧАВАНЕ НА АМИДОАЛКИЛ НАФТОЛИ С
ПОМОЩТА НА ПРАЙСЛЕР НАНОЧАСТИЦИ ВЪРХУ СИЛИЦИЕВ ДИОКСИД

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(Резюме)

Описан е един подобрен „зелен“ метод за синтез на амидоалкил нафтоли чрез „one-pot“ многокомпонентна реакция на арил алдехид, β -нафтол и ацетамид или ацетонитрил (реакция тип Ritter) в присъствието на Прайслер наночастици върху силициев диоксид, като ефективен катализатор.