J IRAN CHEM SOC (2014) 11:653–658
DOI 10.1007/s13738-013-0336-z

ORIGINAL PAPER

Nano silica phosphoric acid: an efficient catalyst for the one-pot synthesis of amidoalkyl naphthols under solvent-free condition

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Received: 1 March 2013 / Accepted: 25 August 2013 / Published online: 6 September 2013

Abstract 1-Amidoalkyl-2-naphthols were prepared via one-pot multi-component reaction of 2-naphthol, aldehydes, and amides in the presence of nano silica phosphoric acid under solvent-free condition at 80 °C. Short reaction times, high yields, and easy work-up are the advantages of this protocol.

Keywords Amidoalkyl naphthol · Multi-component reaction · Heterogeneous catalyst · Solvent-free condition

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 reaction especially the Passerini [1], Biginelli [2], Ugi [3] and Mannich [4] reactions, which have further led to renaissance of MCRs. Nevertheless, great efforts have been made to find and develop new MCRs. In a point of view of the conservation of the environment combining with economic aspects, all chemists demand the application of metal ion-free, environmentally safe and convenient reagents in the multi-component reactions [5]. Amidoalkyl naphthols are precursors for the synthesis of 1-aminomethyl-2-naphthols which exhibit important cardiovascular, bradycardiac [6], and hypertensive [7] activities. Previously, some acid catalysts such as [bmim]HSO_4 [8], cyanuric chloride [9], sulphamic acid [10, 11], silica-supported molybdatophosphoric acid [12], $H_3PW_{12}O_{40}$ [13], $H_4SiW_{12}O_{40}$ [14], I_2 [15], [TEBSA][HSO_4] [16], $KHSO_4$ [17], P_2O_5 [18], silica sulfuric acid [19], zirconyl (IV) chloride [20], $HClO_4{\cdot}SiO_2$ [21] and thiamine hydrochloride [22] were applied.

Silica phosphoric acid (SPA) [23] is an efficient and reusable catalyst. It was prepared by reaction of silica chloride with dry phosphoric acid. It is noted that, silica chloride was prepared via reaction of silica gel and thionyl chloride. By using nano silica gel instead of silica gel, according to above pathway, nano silica phosphoric acid (nano-SPA) was prepared. The particle size of nano-SPA was measured by SEM and TEM photography (Fig. 1).

The acidic capacity of nano-SPA was presented 10.32 mmol g^{-1}. It was determined via titration of 0.2 g of nano-SPA with standard solution of NaOH.

The FT-IR (ATR) spectra of silica chloride, nano-SPA and $H_3PO_4{\bullet}SiO_2$ were shown in Fig. 2. In all ATR spectra, the Si–O–H and Si–O–Si stretching bands are appeared in the range of 900–1,100 cm^{-1}. In silica chloride spectrum, the Si–Cl stretching band is appeared in 700 cm^{-1}. In ATR spectra of nano-SPA and $H_3PO_4{\bullet}SiO_2$, the P–O–H, P=O, P–O stretching bands are appeared in 910–1,040, 1,637 and 2,400–2,800 cm^{-1}, respectively. According to above data,

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The manuscript has been presented at the "1st National Conference on Multi-Component Reaction" in Institute of Science and High Technology and Environmental sciences, Graduate University of Advanced Technology, Kerman, Iran, 2012.

Electronic supplementary material The online version of this article (doi:10.1007/s13738-013-0336-z) contains supplementary material, which is available to authorized users.

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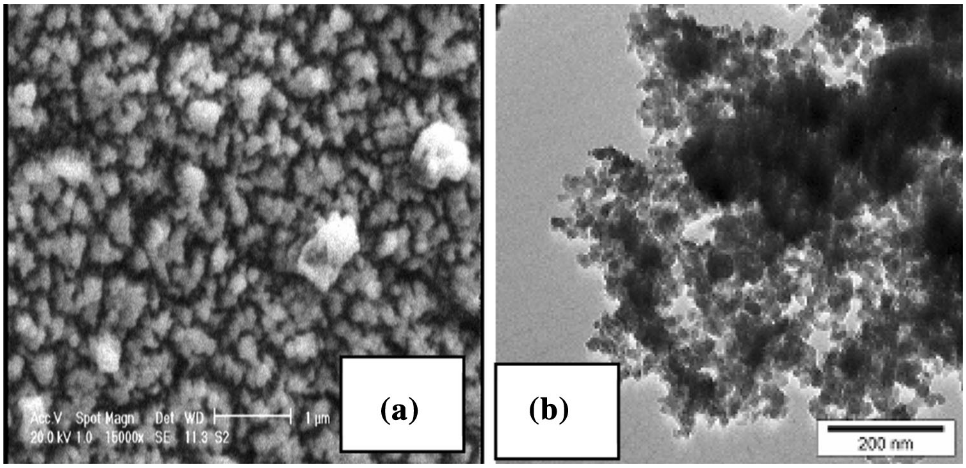


Fig. 1 **a** SEM and **b** TEM photographs of nano-SPA

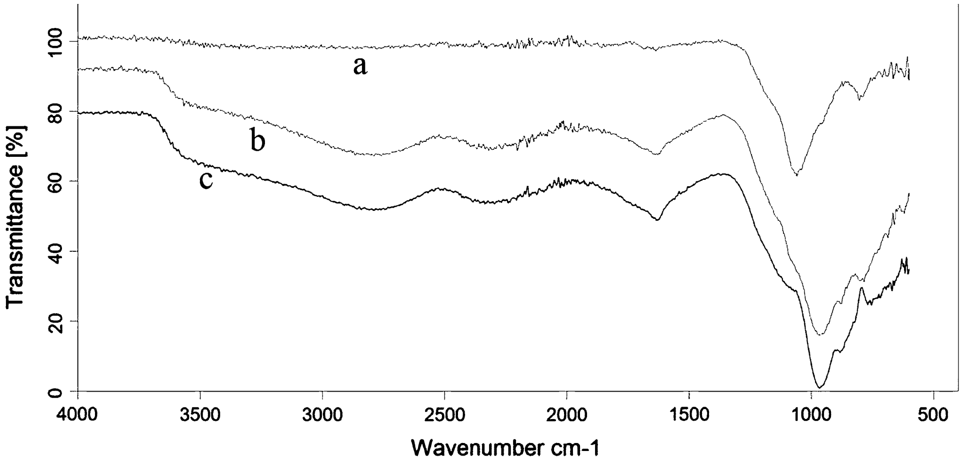


Fig. 2 ATR of **a** silica chloride, **b** nano-SPA and **c**) H_3PO_4•SiO_2

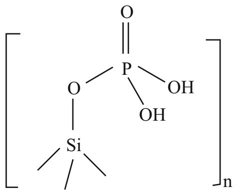
we have suggested the structure for nano-SPA with PO_3H_2 on silica gel (Scheme 1).

Experimental

General

Chemicals were purchased from Sigma–Aldrich and Merck chemical companies and were used without any purification. All products were characterized by their FT-IR, ^{1}H-NMR and comparison of their physical properties with those reported in the literature. FT-IR spectra were recorded on a Bruker, Eqinox 55 spectrometer. In all cases, the ^{1}H-NMR spectra were recorded on a Bruker DRX-400 Avance instrument. Nano-SPA was synthesized according to SPA procedure [23]. The SEM photograph of nano particles was determined with VEGA/TESCAN scanning electron microscope. The TEM photograph was determined by Leo 912AB OMEGA microscope.

Scheme 1 A proposed structure for Nano silica phosphoric acid



Typical procedure for the synthesis of 1-amidoalkyl-2-naphthols

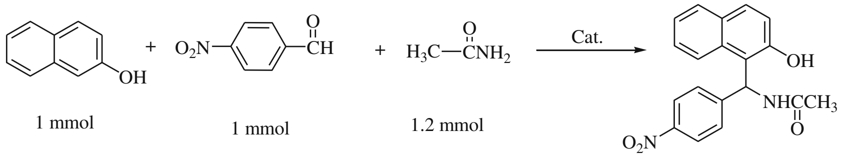
A mixture of an aldehyde (1 mmol), 2-naphthol (1 mmol, 0.144 g), amide (1.2 mmol), and nano-SPA (0.02 g) was heated for 1 h. The progress of the reaction was followed by TLC on silica gel polygram SIL G/UV 254 plates. After completion of the reaction, the mixture was cooled to room temperature. $CHCl_3$ was added to the mixture, filtered to remove the catalyst. By cooling the filtrate, 1-amidoalkyl-2-naphthol was achieved and recrystallized in hot ethanol.

Results and discussion

Initially to find the best reaction conditions, the reaction of 2-naphthol (1 mmol), 4-nitrobenzaldehyde (1 mmol) and acetamide (1.2 mmol) was performed under various conditions and different quantities of SPA and nano-SPA (Table 1). According to the obtained data, the best condition of the reaction was at 80 °C under solvent-free using 0.02 g of nano-SPA (Table 1, entry 10). These conditions are comparable with other applied conditions. The reusability of the SPA catalyst was also examined for six times. After each run, the product was filtered, the solvent was evaporated, the catalyst was washed with $CHCl_3$ and reused. Treatment with $CHCl_3$ removes tars more efficiently from the catalyst surface (Table 1, entries 11–13). The catalyst was reusable, although a gradual decline in activity was observed.

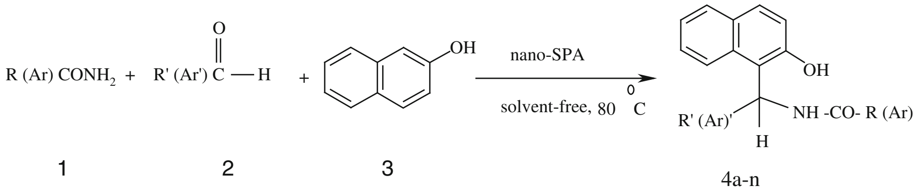
According to the best condition, we have applied 2-naphthol, various aldehydes and amides for the synthesis of 1-amidoalkyl-2-naphthols (Scheme 2; Table 2).

Table 1 Synthesis of *N*-[(2-hydroxynaphthalen-1-yl)-*p*-nitrophenyl-methyl]acetamide under various conditions



Entry	Catalyst (g)	Condition Solvent/T °C	Time (h)/yield (%)^a	References
1	SPA (0.05)	S. F./80	4/96	–
2	SPA (0.06)	S. F./80	1/98	–
3	SPA (0.06)	H_2O/80	3/90	–
4	SPA (0.06)	S. F./R.T.	12/0	–
5	SPA (0.06)	EtOAc/80	2/98	–
6	SPA (0.06)	DMSO/80	4/80	–
7	SPA (0.06)	n-Hexan/80	4/82	–
8	SPA (0.06)	EtOH/80	4/80	–
9	SPA (0.06)	MeOH/80	4/75	–
10	Nano-SPA (0.02)	S. F./80	1/98	–
11	Nano-SPA (0.02), 2nd run	S. F./80	2/92	–
12	Nano-SPA (0.02), 3rd run	S. F./80	2/81	–
13	Nano-SPA (0.02), 4th run	S. F./80	2/75	–
14	Nano-SPA (0.02), 5th run	S. F./80	2/64	–
15	Nano-SPA (0.02), 6th run	S. F./80	2/52	–
16	$HClO_4/SiO_2$	S. F./110	0.5/95	[21]
17	$HClO_4/SiO_2$	MW	0.2/91	[21]
18	P_2O_5	S. F./60	0.1/96	[18]
19	[TEBSA][HSO_4]	S. F./120	0.15/88	[16]
20	$KHSO_4$	S. F./100	0.5/96	[17]
21	TCT	S. F./100	0.7/93	[9]
22	$H_3PW_{12}O_{40}$	Et_4NCl/100	1.4/95	[13]
23	$H_4SiW_{12}O_{40}$	S.F./110	0.25/82	[14]
24	$H_3PMo_{12}O_{40}\bullet xH_2O/SiO_2$	S.F./120	0.25/90	[12]

^{a} Conversion yields



Scheme 2 Synthesis of 1-amidoalkyl-2-naphthols in the presence of Nano silica phosphoric acid at 80 °C under solvent free condition

Table 2 Synthesis of 1-amidoalkyl-2-naphthols in the presence of nano-SPA in solvent-free at 80 °C

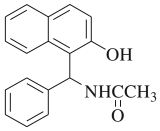
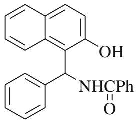
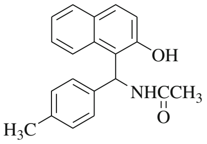
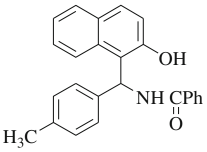
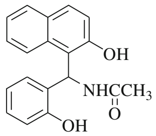
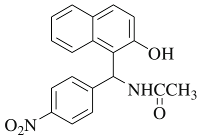
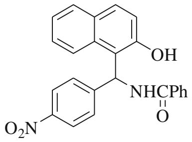
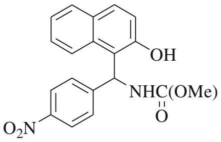
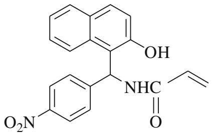
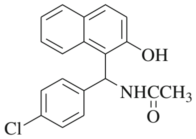
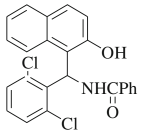
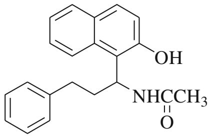
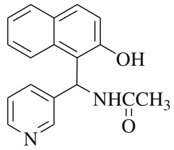
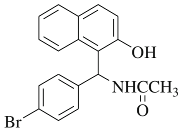
Entry	R′ (Ar′)	R (Ar)	Product	Time (min)	Yield[a]	M.P. °C		References
						Found	Reported	
1	C_6H_5	CH_3		55	98	250–252	243–245	[9]
2	C_6H_5	C_6H_5		50	95	229–131	230–232	[9, 26]
3	4-MeC_6H_4	CH_3		60	90	224–226	222–223	[24]
4	4-MeC_6H_4	C_6H_5		45	91	226–228	226–228	[26]
5	2-HOC_6H_4	CH_3		90	80	214–216		[26]
6	4-$O_2NC_6H_4$	CH_3		60	96	242–243	237–238	[18]
7	4-$O_2NC_6H_4$	C_6H_5		30	97	236–238	228–229	[18]
8	4-$O_2NC_6H_4$	CH_3O		55	96	210–212	205–207	[25]
9	4-$O_2NC_6H_4$	$H_2C{=}CH$		15	91	231–233		[26]

Table 2 continued

Entry	R′ (Ar′)	R (Ar)	Product	Time (min)	Yield[a]	M.P. °C		References
						Found	Reported	
10	4-ClC_6H_4	CH_3		70	93	230–231	229–231	[9]
11	2,6-$Cl_2C_6H_3$	C_6H_5		90	94	215–217		[26]
12	$C_6H_5CH_2CH_2$	CH_3		170	83	190–192		[26]
13	3-pyridyl	CH_3		120	98	192–194		[26]
14	4-BrC_6H_4	CH_3		80	90	232–233	230–232	[9]

The ratio of 2-naphthol (mmol): aldehyde (mmol):amide (mmol): nano-SPA (g) is 1:1:1.2:0.02

[a] Isolated yield

Aldehydes containing electron withdrawing groups such as 4-nitrobenzaldehyde were reacted in higher yields and shorter reaction times (Table 2, entries 6–9). On the contrary, aldehydes with electron releasing groups were reacted in lower yields and longer reaction times (Table 2, entry 5). Aliphatic aldehydes were also examined, but their yields were low in comparison to the products from aromatic aldehydes. The reactions of urea or thiourea with acetamide and 2-naphthol were examined, but no corresponding products were produced.

Conclusions

In conclusion, a highly efficient synthesis of amidoalkyl naphthols via multi-component condensation of aromatic aldehydes, β-naphthol and amides catalyzed by nano-SPA is reported. This method offers significant advantages, such as high conversions, easy handling, cleaner reaction profile and shorter reaction times which makes it a useful and attractive process for the rapid synthesis of substituted amidoalkyl naphthols.

Acknowledgments The authors are grateful to University of Kashan for supporting this work by Grant No. (159189/5).

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