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$NaHSO_4$ supported on silica: An alternative and efficient catalyst for green synthesis of amidoalkyl naphthols under ultrasound irradiation

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ABSTRACT

An efficient and environment-friendly approach for the synthesis of amidoalkyl naphthols via multicomponent one-pot reaction of β-naphthol, aldehyde and urea/amide is herein described employing neat reaction conditions under ultrasound irradiations using SiO_2-$NaHSO_4$ as inexpensive solid catalyst. The present approach offers several advantages such as short reaction times, higher yields, eco-friendly reaction condition, easy purification and availability of the catalyst.

KEYWORDS

Multicomponent reaction;
Ultrasonic irradiation;
SiO_2-$NaHSO_4$;
Amidoalkyl naphthol.

INTRODUCTION

One pot multicomponent reactions (MCRs) have attracted considerable interest owing to their exceptional synthetic efficiency. The structure of the reaction product can easily be diversified by the systematic variation of each input. Moreover, the starting materials are either commercially available or easy to prepare[1]. Multi-component reactions (MCRs) in heterocyclic synthesis is one of the most important area in the synthetic organic chemistry and medicinal chemistry because they are one-pot processes bringing together three or more components and show high atom economy and high selectivity[1a]. Recently organic syntheses involving multi-component condensation strategy attained greater value, as the target molecules are often obtained in a single step rather than multiple steps which minimize the tedious work-up procedures and environmental hazardous wastes. MCRs are performed without the need to isolate any intermediate and save both energy and raw materials and also reduce time. Compounds containing 1,3-amino-oxygenated functional groups are frequently found in biologically active natural products and potent drugs such as nucleoside antibiotics and HIV protease inhibitors[2]. Also it is reported that amidoalkyl naphthols (as 1,3-amino-oxygenated compounds) can convert to important biologically active aminoalkyl naphthol derivatives by an amide hydrolysis reaction[3]. Thus the synthesis of amidoalkyl naphthols is of paramount importance in organic synthesis.

A survey of literature shows importance using ultrasound irradiation in chemical processes. The use of ultrasound to promote chemical reactions is called sonochemistry. Sonochemistry is a new trend in organic chemistry, offering a versatile and facile pathway for a large variety of syntheses. Thus, the use of Sonication allows: short reaction times, high yields, improved selectivity, milder conditions and

eco-friendly[4]. Ultrasonic-assisted organic synthesis (UAOS) as a green synthetic approach is a powerful technique that is being used more and more to accelerate organic reactions[5]. Cella and Stefani have recently published a review concerning to the use of ultrasound in heterocyclic chemistry that shows importance sonochemistry in synthesis of heterocyclic compounds[6].

Amidoalkyl naphthols can be prepared by the condensation of aromatic aldehydes, 2-naphthol and amides, urea or acetonitrile in the presence of a Lewis or Brønsted acid catalysts. Several methods have been documented in the literature for synthesis of these compounds such as montmorillonite K10 clay[7], $Ce(SO_4)_2$[8], $K_5CoW_{12}O_{40}.3H_2O$[9], *p*-TSA[10], sulfamic acid[11], ionic liquids[12], I_2[13], $Al(H_2PO_4)_3$[14], $Fe(HSO_4)_3$[15], $Yb(OTf)_3$[16], wet-TCT[17], Al_2O_3-$HClO_4$[18], Silica chloride (SiO_2-Cl)[19], indium (III) chloride[20], $Sr(OTf)_2$[21], P_2O_5[22], $H_4SiW_{12}O_{40}$[23], N, N, N^1, N^1-Tetrabromobenzene-1,3-disulfonamide (TBBDA)[24], trityl chloride[25] and bismuth (III) nitrate pentahydrate[26].

In this work, we have reported the application of the SiO_2-$NaHSO_4$ materials as heterogeneous catalyst for synthesis of structurally diverse amidoalkyl naphthols under environmentally ultrasound irradiations conditions Scheme 1.

EXPERIMENTAL

Chemicals were obtained from Merck and Sigma-Aldrich and used without further purification. The products (4a-s) were isolated and characterized by physical and spectral data. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-300 MHz spectrometers with 7-10mM solutions in $CDCl_3$ in the presence of tetramethylsilane as internal standard. IR spectra were recorded using a Perkin-Elmer 843 spectrometer with KBr plates. Sonication was performed in Falc-Italy LBS2-4.5 ultrasonic cleaner (with a frequency of 25 kHz). Melting points were determined on Electro thermal 9100, and are not corrected.

Synthesis of amidoalkyl naphthols: General procedure

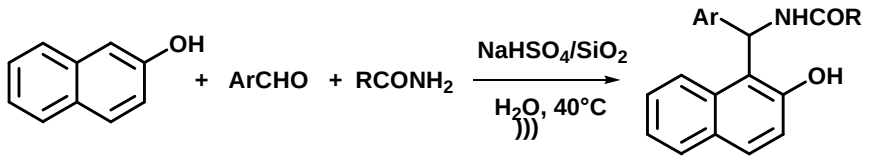
To a mixture of an aldehyde (1 mmol), 2-naphtol (1 mmol), amide (1.2 mmol) and water (10 mL) was added $NaHSO_4/SiO_2$ (50 mg) and the reaction mixture was exposed to ultrasonic irradiation at 40 °C for 10 min. The progress of the reaction was followed by TLC. After completion of the reaction, the reaction mixture was diluted with ethanol (5 mL) and stirred for 10 min in 80°C. The solid (catalyst) were collected by filtration and the residue was kept at room temperature and the resulting crystalline product was collected by filtration. The product was found to be pure and no further purification was necessary.

(a) Compound 4e

IR (KBr): 3380, 3053, 2232, 1629, 1529, 1513, 1476, 1440, 1336, 1283, 1248, 1067, 883, 859, 825 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.99 (3H, s), 7.13 (1H, d, J= 7.94 Hz), 7.18-7.40 (5H, m), 7.69-7.82 (5H, m), 8.50 (1H, d, J= 7.94 Hz), 10.05 (1H, sbr); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 22.48, 47.81, 108.73, 117.87, 118.33, 118.92, 122.52, 122.88, 126.61, 126.89, 128.38, 128.61, 129.74, 131.93, 132.15, 148.88, 153.25, 169.58; Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.95; H, 5.06, N, 8.86. Found: C, 75.90; H, 5.11, N, 8.78.

(b) Compound 4m

IR (KBr): 3241, 3063, 2229, 1644, 1591, 1519, 1459, 1433, 1402, 1247, 1240, 1084, 962, 839, 815 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.22 (1H, d, 8.42 Hz), 7.28-7.97 (15H, m), 8.67 (1H, d, J= 8.42 Hz), 10.33 (1H, sbr); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 36.42, 116.33, 117.68, 118.43, 118.95, 123.16, 123.98, 124.71, 127.16, 127.32, 127.35, 128.40, 128.67, 128.77, 129.51, 130.61, 130.71, 132.45, 148.01, 151.52, 168.52; Anal. Calcd for $C_{25}H_{18}N_2O_2$: C, 79.36; H, 4.76, N, 7.41. Found: C, 79.22; H, 4.87, N, 7.83.



Scheme 1

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(c) Compound 4r

IR (KBr): 3306, 3067, 2231, 1664, 1593, 1520, 1505, 1461, 1435, 1403, 1250, 1242, 1146, 965, 842, 817 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ= 6.85 (1H, s), 7.44-7.65 (5H, m), 7.79-7.97 (5H, m), 8.66 (1H, d, J= 8.43 Hz), 10.15 (1H, sbr); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 36.42, 108.82, 116.32, 117.67, 123.15, 124.71, 124.73, 127.16, 128.68, 128.76, 129.51, 130.61, 130.71, 132.45, 148.00, 150.98, 159.98; Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.92; H, 4.73, N, 13.25. Found: C, 72.11; H, 4.67, N, 13.34.

RESULTS AND DISCUSSION

Initially, we sought a mild and convenient method for the synthesis of amidoalkyl naphthols. At first, we chose 4-chlorobenzaldehyde, 2-naphthol and acetamide (mole rate 1:1:1.2) under ultrasonic irradiation as model reactants and examined the effect of the amount of $NaHSO_4/SiO_2$. According to this data, the optimum amount of catalyst was 50 mg. Further increasing the amount of catalyst did not improve the yield and the reaction time. In order to evaluate the effect of solvent, we examined different solvents under room temperature for the above model reaction. The outstanding feature of data that can be elicited from results, water is best solvent for this reaction under ultrasonic irradiation.

In order to show the effect of ultrasonic irradiation in these reactions, the synthesis of (4b) was investigated as a typical example in the presence of 10, 20, 30, 40 and 50 mg of $NaHSO_4/SiO_2$ with and without ultrasonic irradiation. The reaction rates and yields were dramatically enhanced by ultrasound. The rate enhancement under ultrasound may be attributed to the cavitation, activation of the catalyst and the intercalation of guest molecules into host nanoreactor by sonic waves. In the absence of sonic waves, the products were formed in moderate yields unless the temperature was increased. The role of ultrasound in promoting the rapid and green synthesis of amidoalkyl naphthol derivatives is evident from the fact that the corresponding reactions under stirred conditions without ultrasound (silent reactions) needed much longer time for promotion, in all cases with lowered yields. Based on the results of this

TABLE 1 : $NaHSO_4/SiO_2$ catalyzed synthesis of amidoalkyl naphthols under ultrasonic irradiation

Entry	Ar	R	Product	Time (min)	Yield (%)	Mp (°C)	
						Found	Reported
1	C_6H_5	CH_3	4a	10	94	242-243	242-244
2	4-ClC_6H_5	CH_3	4b	10	94	230-231	228-229
3	4-BrC_6H_5	CH_3	4c	10	95	232-234	228-230
4	4-FC_6H_5	CH_3	4d	10	96	210-212	203-205
5	4-CNC_6H_5	CH_3	4e	12	92	260-262	260-262
6	3-$NO_2C_6H_5$	CH_3	4f	8	96	212-214	212-215
7	3-$MeOC_6H_5$	CH_3	4g	14	90	204-205	203-205
8	2-ClC_6H_5	CH_3	4h	8	94	195-197	194-196
9	C_6H_5	Ph	4i	10	90	230-232	234-236
10	4-MeC_6H_5	Ph	4j	12	90	204-205	192-193
11	4-ClC_6H_5	Ph	4k	10	92	176-177	177-178
12	4-FC_6H_5	Ph	4l	10	93	195-196	193-194
13	4-CNC_6H_5	Ph	4m	12	92	176-178	176-178
14	3-$NO_2C_6H_5$	Ph	4n	8	95	215-216	216-217
15	C_6H_5	NH_2	4o	14	90	231-232	230-232
16	4-ClC_6H_5	NH_2	4p	12	91	168-170	168-169
17	4-BrC_6H_5	NH_2	4q	12	92	174-176	170-172
18	4-CNC_6H_5	NH_2	4r	14	90	333-335	330-332
19	3-$NO_2C_6H_5$	NH_2	4s	8	95	254-256	255-259

study, it shows that the ultrasound irradiation improves the reaction times and yields.

Having established optimal reaction conditions, we probed the generality of process TABLE 1. The three-component coupling reactions of benzaldehyde, 2-naphthol and amidein the presence of 50 mg of $NaHSO_4/SiO_2$ in water at 40 °C was conducted under ultrasound irradiation. The reaction worked well with electron-withdrawing as well as electron-donating groups, giving various amidoalkyl naphthol derivatives in high yields. As shown in TABLE 1, the method is general and includes a variety of functional groups.

In summary, a novel and highly efficient methodology for the synthesis of amidoalkyl naphthols by condensation reaction of aldehydes, 2-naphtol and acetamide or benzamide or urea in the presence of catalytic amounts of $NaHSO_4/SiO_2$ under ultrasonic irradiation is reported. This protocol describes a very fast, user friendly, 'green' and low cost procedure for the synthesis of these products.

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