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One-pot synthesis of amidoalkyl naphthols using $NaHSO_4.SiO_2$ as an efficient and recyclable heterogeneous catalyst

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An efficient synthesis of amidoalkyl naphthols using silica supported sodium hydrogen sulphate as heterogeneous catalyst under a thermal solvent-free green procedure is described. This simple protocol offer advantages such as shorter reaction times, simple work-up, excellent yield, and recovery and reusability of the catalyst.

Key Words: $NaHSO_4.SiO_2$; amidoalkyl naphthol; multi-component reaction; heterogeneous catalyst, amide.

Introduction

Multi-component reactions have attracted considerable attention in organic syntheses as they can produce the target products in a single operation without isolating the intermediates and thus reducing the reaction times and energy.[1,2] Heterogeneous catalysts have gained much importance in recent years due to economic and environmental considerations.[3] These catalysts are generally less expensive, highly reactive, eco-friendly, and convenient to handle, with enhanced reaction times, greater selectivity, simple workup, and recoverability of catalysts.[4–11]

The preparation of 1-amidoalkyl-2-naphthols can be carried out by condensation of aryl aldehydes, 2-naphthol, and acetonitrile or amide in the presence of Lewis or Brønsted acid catalysts such as montmorillonite K10 clay,[12] $Ce(SO_4)_2$,[13] iodine,[14] $K_5CoW_{12}O_{40}.3H_2O$,[15] *p*-TSA,[16] sulphamic acid,[17] cation-exchanged resins,[18] silica sulphuric acid,[19] SiO_2-$FeCl_3$,[20] and SiO_2-$HClO_4$.[21] It is noteworthy that 1-amidomethyl-2-naphthols can convert to important biologically active 1-aminomethyl-2-naphthol derivatives[22,23] by amide

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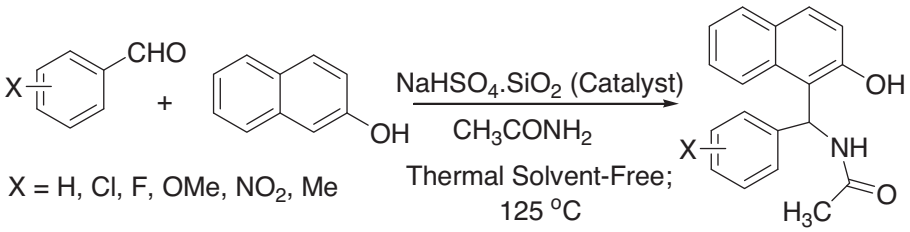
hydrolysis reaction. Compounds bearing 1,3-amino oxygenated moieties are frequently found in various bioactive natural products and important drug molecules.[24]

However, many of these methodologies suffer from the drawback of green chemistry[13,14,25] and have been associated with several shortcomings such as long reaction times, expensive reagents, low product yields, and difficulty in recovery and reusability of the catalysts. Due to these problems, development of an efficient and versatile method for the preparation of amidoalkyl-2-naphthols is an important aspect. This is an active on-going research area and there is scope for further improvement towards mild reaction conditions and improved yields. Recently, Das et al. prepared these products via a Ritter-type reaction in the presence of triflic acid as a strong and non-reusable acid catalyst.[26] The reaction was completed within 1.5-6 h and the yields were 50%-91%.[26] Herein, we describe practical and inexpensive methods for the preparation of 1-amidoalkyl-2-naphthol derivatives via multi-component reactions in the presence of $NaHSO_4.SiO_2$ as catalyst in a short reaction time (Scheme 1).



Scheme 1. Preparation of amidoalkyl naphthols.

Experimental

Silica supported sodium hydrogen sulphate can easily be prepared from the readily available inexpensive ingredients $NaHSO_4.H_2O$ and silica gel.[27]

General procedure: silica supported sodium hydrogen sulphate catalyzed preparation of amidoalkyl naphthols: To a mixture of 2-naphthol (10 mmol), aldehydes (10 mmol), and acetamide (12 mmol) was added $NaHSO_4.SiO_2$ (200 mg, 0.6 mmol H^+)[27]. The mixture was stirred at 120 °C in an oil bath and the reaction was followed by TLC. After completion of the reaction, the mass was cooled to 25 °C; then the solid residue was dissolved in acetone and the mixture stirred for 5 min. The catalyst was recovered and washed with chloroform, and dried in an oven at 100 °C. Then filtrate solution was evaporated under reduced pressure and the solid so obtained was recrystallized in aqueous EtOH (15%). The desired pure product(s) was characterized by comparison of its physical data with those of known compounds.[12–21] The spectral data of some representative amidoalkyl naphthols are given below:

***N*-[(4-Methyl phenyl)-(2-hydroxy-naphthalen-1-yl)methyl]acetamide (Table 2, Entry 2):** ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.96 (s, 3H), 2.21 (s, 3H), 7.08-7.03 (m, 5H), 7.19 (d, J = 8.8 Hz, 1H), 7.24 (t, J = 7.1 Hz, 1H), 7.34 (m, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.82 (br, 1H), 8.36 (d, J =8.1 Hz, 1H), 9.91 (s, 1H) ppm; ^{13}C-NMR (125 MHz, DMSO-d_6): 20.4, 22.6, 47.6, 118.4, 118.9, 122.2, 123.1, 125.9, 126.1, 128.3, 128.4, 128.9, 132.2, 134.9, 139.4, 143.3, 152.9, 168.9 ppm; IR (KBr, cm^{-1}): 3419, 3316, 3070, 1621, 1595, 1561, 1514, 1466, 1392, 1283, 1202, 1141, 1051, 939, 884, 784, 745, 712.; MS: m/z

(%) = 305 (M^+, 21), 246 (29), 245 (50), 231 (100), 232 (31), 202 (16), 115 (10); Anal. Calcd. for $C_{20}H_{19}NO_2$: C: 78.66; H: 6.27; N: 4.59. Found: C: 78.72; H: 6.21; N: 4.63.

***N*-[(3-Fluoro phenyl)-(2-hydroxy naphthalen-1-yl)-methyl]-acetamide (Table 2, Entry 9):** ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.98 (s, 3H), 6.98-6.92 (m, 3H), 7.12 (d, J = 8.3 Hz, 1H), 7.27-7.19 (m, 3H), 7.37 (t, J = 7.3 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.84 (brd, 1H), 8.44 (d, J = 8.2 Hz, 1H), 10.01 (s, 1H) ppm; ^{13}C-NMR (125 MHz, DMSO-d_6): 22.5, 47.5, 112.5 (d, $^2J_{C-F}$ = 22.1 Hz), 112.7 (d, $^2J_{C-F}$ = 20.9 Hz), 118.3, 118.4, 122.1 (d, $^4J_{C-F}$ = 2.5 Hz), 122.4, 122.9, 126.4, 128.3, 128.5, 129.4, 129.8 (d, $^3J_{C-F}$ = 8.1 Hz), 132.1, 145.9 (d, $^3J_{C-F}$ = 6.6 Hz), 153.1, 162.0 (d, $^1J_{C-F}$ = 241.2 Hz), 169.3 ppm; IR (KBr, cm^{-1}): 3410, 3160, 1640, 1589, 1545, 1484, 1439, 1335, 1280, 1064, 989, 814, 760, 743; MS: m/z (%) = 310 (5), 309 (M^+, 21), 251 (9), 250 (52), 249 (100), 231 (14), 220 (16), 122 (7), 115 (9); Anal. Calcd. for $C_{19}H_{16}FNO_2$: C: 73.77; H: 5.21; N: 4.53. Found: C: 73.74; H: 5.25; N: 4.48.

***N*-[(2,5-Dimethoxy phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl]-acetamide (Table 2, Entry 12):** ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.88 (s, 3H), 3.48 (s, 3H), 3.64 (s, 3H), 6.77-6.72 (m, 2H), 7.23-7.10 (m, 4H), 7.39 (s, 1H), 7.73-7.66 (m, 2H), 8.27-8.15 (m, 2H), 9.75 (s, 1H) ppm; ^{13}C-NMR (125 MHz, DMSO-d_6): 22.5, 44.4, 55.2, 55.9, 111.1, 111.9, 115.7, 118.5, 118.9, 122.0, 123.2, 125.7, 128.1, 128.6, 131.7, 132.4, 150.7, 152.7, 153.1, 168.1 ppm; IR (KBr, cm^{-1}): 3365, 3174, 3002, 2939, 1614, 1577, 1497, 1436, 1370, 1317, 1277, 1218, 1084, 1052, 819, 797, 727; MS: m/z (%) = 351 (M^+, 18), 308 (5), 276 (6), 262 (36), 261 (100), 218 (16), 144 (7), 115 (8); Anal. Calcd for $C_{21}H_{21}NO_4$: C: 71.78; H: 6.02; N: 3.99. Found: C: 71.73; H: 5.93; N: 4.08.

Results and discussion

To choose an effective catalyst, we prepared *N*-[phenyl-(2-hydroxynaphthalen-1-yl) methyl] acetamide from the reaction of benzaldehyde, 2-naphthol, and acetamide in the presence of different catalysts such as ZnO, $NaHSO_4.H_2O$, Na_2SO_4, and $NaHSO_4.SiO_2$ (50 mg) at 120 °C under solvent-free conditions (Table 1). Table 1 clearly demonstrates that $NaHSO_4.SiO_2$ is an effective catalyst in terms of reaction time and yield of obtained product.

Table 1. Reaction of benzaldehyde, 2-naphthol and acetamide in different catalytic conditions.[a]

Entry	Catalyst	Time	Yield (%)[b]
1	None	24 h	-
2	ZnO	5 h	57
3	$NaHSO_4.H_2O$	15 min	84
4	Na_2SO_4	1 h	-
5	$NaHSO_4.SiO_2$	5 min	95

[a] the reaction was carried out under thermal solvent-free conditions in an oil bath at 120 °C; molar ratio benzaldehyde/2-naphthol/acetamide/catalyst (1/1/1.2/50 mg)

[b] Isolated yields after purification of product

The effective amount of silica supported sodium hydrogen sulphate catalyst was also investigated. Generally, the reaction rate and yield increased with the amount of catalyst. It was found that 20 mg of catalyst was the appropriate amount for the reaction. Smaller amounts gave a low yield even after a long reaction time, and greater amounts did not cause an obvious increase in the yield of product. Hence, the optimal amount of catalyst chosen was 20 mg in the subsequent reactions (Figure).

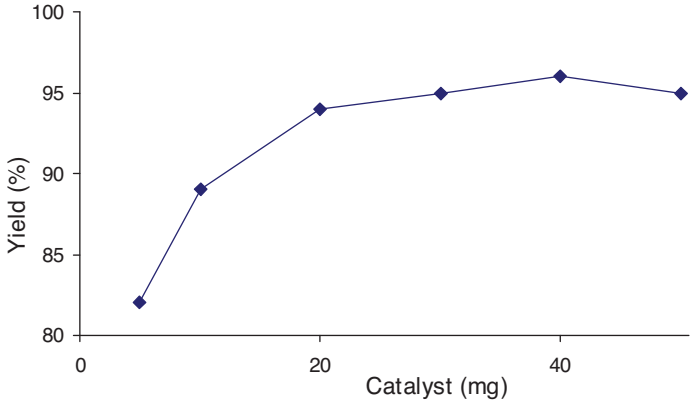


Figure. Optimization of the catalyst.

Thus, we prepared a range of amidoalkyl naphthols under the optimized reaction conditions: 2-naphthol, arylaldehydes (1:1), and acetamide (1.2 mmol) in the presence of silica supported sodium hydrogen sulphate (20 mg) (Table 2).

In all cases, aromatic aldehydes with substituents carrying either electro-donating or electron-withdrawing groups reacted successfully and gave the products in high yields. It was shown that the aromatic aldehydes with electron withdrawing groups reacted faster than the aromatic aldehydes with electron releasing group as would be expected (Table 2). Aromatic aldehydes with steric hindrance such as 2-chloro bezaldehydes reacted at long reaction times. Aliphatic aldehydes reacted sluggishly and gave side products; hence the desired product could not be isolated.

As reported in the literature,[16] the reaction of 2-naphthol with aromatic aldehydes in the presence of acid catalyst is known to give *ortho*-quinone methides (*o*-QMs). The same *o*-QMs, generated in situ, have been reacted with acetamide to form 1-amidoalkyl-2-naphthol derivatives. A possible reasonable explanation for this mechanism can be given by considering that the nucleophilic addition to *o*-QMs intermediate is favourable via conjugate addition on the α,β-unsaturated carbonyl group that aromatizes a ring of this intermediate (Scheme 2). The electron withdrawing groups substituted on benzaldehyde in *o*-QMs intermediate increase the rate of the 1,4-nucleophilic addition reaction because alkenes LUMO is at lower energy near withdrawing groups than electron donating groups.[28]

To test the merit of the present work in comparison with results in the literature, we compared results of $NaHSO_4.SiO_2$ with montmorillonite K10 clay,[12] $Ce(SO_4)_2$,[13] iodine,[14] $K_5CoW_{12}O_{40}.3H_2O$,[15] *p*-TSA,[16] sulphamic acid,[17] cation-exchanged resins,[18] silica sulphuric acid, [19] SiO_2-$HClO_4$,[21] and TfOH [26] in the synthesis of 1-amidomethyl-2-naphthol derivatives. As shown in Table 3, $NaHSO_4.SiO_2$ can act as an effective catalyst with respect to reaction times and yields of the obtained products. Thus, the present protocol with $NaHSO_4.SiO_2$ catalyst is convincingly superior to the recently reported catalytic methods.

Table 2. Preparation of 1-amidoalkyl-2-naphthols.

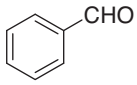
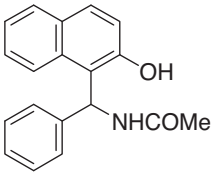
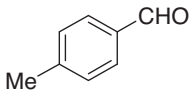
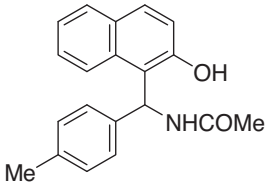
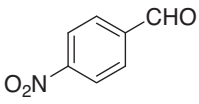
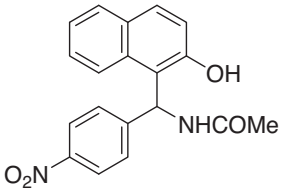
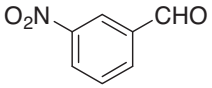
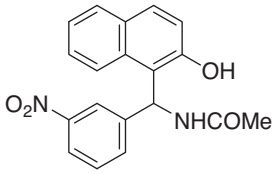
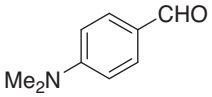
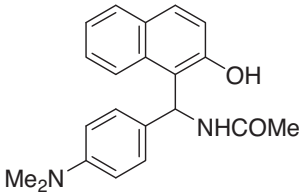
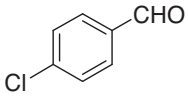
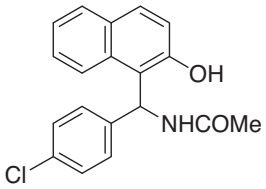
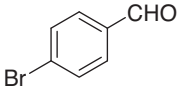
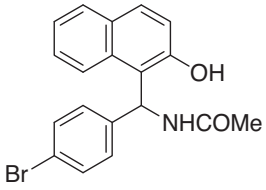
Entry	Aldehyde	Product	Time (min)/ Yield (%)[a]	mp °C (Lit mp)
1			9 / (91-95)[b]	245-246 (241-243)[13]
2			19 / 90	222-223 (222-223)[21]
3			6 / 97	247-249 (248-250)[21]
4			5 / 97	241-242 (182-184)[13]
5			45 / 54	123-125 (78-79)[13]
6			7 / 94	223-225 (224-227)[13]
7			8 / 86	227-229 (228-230)[12]

Table 2. Continued.

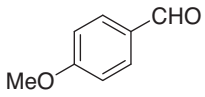
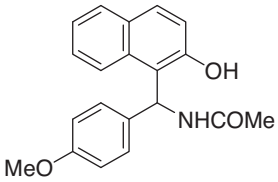
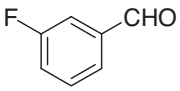
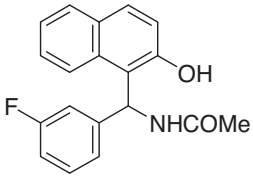
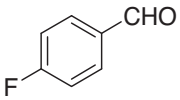
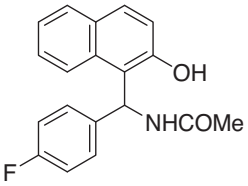
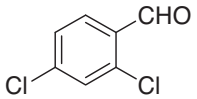
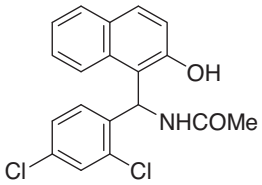
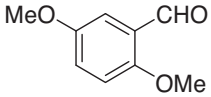
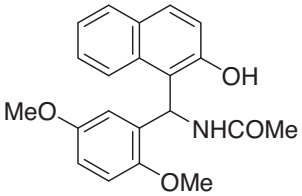
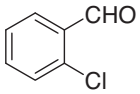
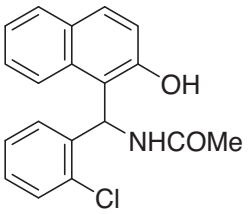
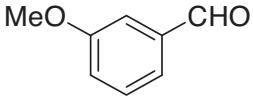
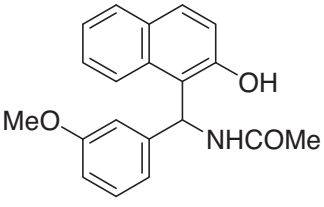
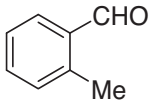
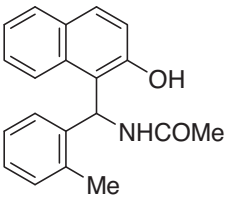
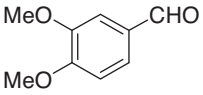
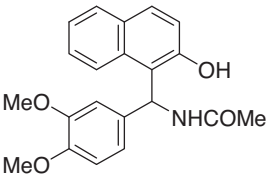
Entry	Aldehyde	Product	Time (min)/ Yield (%)[a]	mp °C (Lit mp)
8			33 / 73	185-187 (184-186)[13]
9			6 / 93	248-249 (248-249)[21]
10			9 / 93	230-232 (209-210)[13]
11			7 / 93	201-203 (198-199)[13]
12			19 / 89	251-253 (251-253)[21]
13			23 / 90	213-215 (194-196)[17]
14			19 / 87	202-204 (203-205)[12]

Table 2. Continued.

Entry	Aldehyde	Product	Time (min)/ Yield (%)[a]	mp °C (Lit mp)
15			27 / 85	199-202 (200-202)[17]
16			25/ 67	235-237 (235-236)[13]

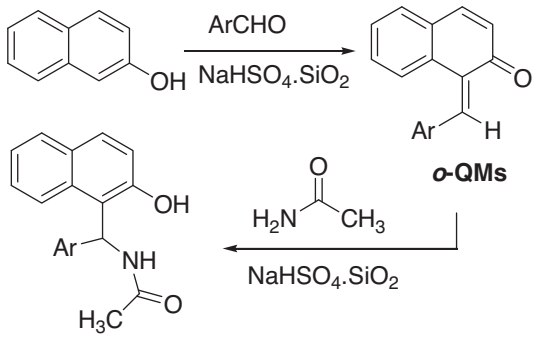
[a]Yields refer to the pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of IR and NMR spectra with authentic samples.[12-21]
[b]Yields after recovery of the catalyst 5 times.

Table 3. Comparison results of $NaHSO_4.SiO_2$ with other catalysts reported in the literature.[a]

Entry	Catalyst	Catalyst; conditions	Time	Yield (%)
1	$Ce(SO_4)_2$	100 mol%; acetonitrile; under reflux	36 h	72
2	I_2	5 mol%; solvent-free, 125 °C	5.5 h	85
3	Montmorillonite K10 clay	0.1 g; solvent-free, 125 °C	1.5 h	89
4	$K_5CoW_{12}O_{40}.3H_2O$	0.01 (1 mol %); solvent-free, 125 °C	2 h	90
5	cation-exchanged resins	0.25 g; solvent-free, 110 °C	20 min	81
6	*p*-TSA	10 mol%; solvent-free, 125 °C	5 h	88
7	sulphamic acid	50 mol %; solvent-free, ultrasonic; 28-30 °C	15 min	89
8	silica sulphuric acid	0.02 g; solvent-free, r.t.	2 h	85
9	SiO_2-$HClO_4$	0.006 g (0.6 mol %); solvent-free, 125 °C	40 min	89
10	TfOH	10 mol%; acetonitrile; under reflux	3 h	89
11	$NaHSO_4.SiO_2$	0.02 g (6 mol %); solvent-free, 125 °C	9 min	95

[a]Based on 2-naphthol (1 equiv.), benzaldehyde (1 equiv.) and acetamide (1.2 equiv.)

The recyclability of the catalyst in the reaction of benzaldehyde (10 mmol), 2-naphthol (10 mmol), and acetamide (12 mmol) in the presence of $NaHSO_4.SiO_2$ (0.2 g) was checked (Table 2, Entry 1). The separated catalyst can be reused after washing with $CHCl_3$ and drying at 100 °C. The catalyst was recovered in excellent yields and the catalyst was used in the mentioned reaction 5 times. It showed the same activity as fresh catalyst without any loss of activity.



Scheme 2. Suggested mechanism for preparation of the amidoalkyl naphthol.

Conclusion

We have demonstrated that silica supported sodium hydrogen sulphate is a new efficient and green catalyst for synthesis of 1-amidoalkyl-2-naphthols. 1-Amidoalkyl-2-naphthol derivatives were prepared via a 3-component reaction of an aryl aldehydes, 2-naphthol, and acetamide in the presence of a catalytic amount of silica supported sodium hydrogen sulphate. This thermal solvent-free green procedure offers such advantages as shorter reaction times, simple work-up, environmental friendliness, excellent yield, cost effective recovery, and reusability of the catalyst a number of times without appreciable loss of activity.

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