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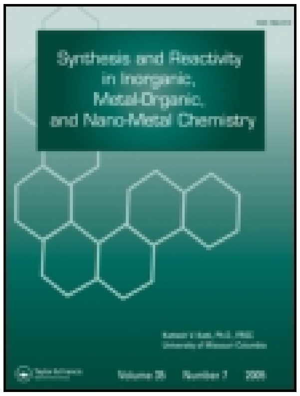

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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$SbCl_3$-SiO_2 Catalyzed Simple and Efficient One-Pot Synthesis of 1-Amidoalkyl-2-Naphthols Under Solvent-Free Conditions

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Silica-supported antimony trichloride ($SbCl_3$-SiO_2) was found to be an inexpensive and effective catalyst for the one-pot three-component synthesis of 1-amidoalkyl-2-naphthols in high yields. The main advantages of the present approach are short reaction times, clean reaction profiles, and simple experimental and work-up procedures.

Keywords 1-amidoalkyl-2-naphthols, heterogeneous catalyst, one-pot reaction, silica-supported antimony trichloride ($SbCl_3$-SiO_2), solvent-free

INTRODUCTION

1-amidoalkyl-2-naphthols have received much attention because of their easy transformation to 1-aminoalkyl-2-naphthols as an important class of bioactive compounds, by amide hydrolysis reaction. 1-aminoalkyl-2-naphthols have been regularly used as hypotensive and bradycardiac agents.[1] 1-Amidoalkyl-2-naphthols can be also converted to 1,3-oxazine derivatives.[2] 1,3-oxazines have potentially different biological activities such as antibiotic,[3] antitumor,[4] analgesic,[5] anticonvulsant,[6] antipsychotic,[7] antimalarial,[8] antianginal,[9] antihypertensive,[10] and antirheumatic properties.[11] Synthesis of 1-amidoalkyl-2-naphthols is usually done via one-pot three-component condensation of arylaldehydes, 2-naphthol and amide derivatives, or acetonitrile. Several Lewis and Brønsted acids have been used for this reaction including $Ce(SO_4)_2$, Montmorillonite K-10, iodine, cation-exchanged resins, $NaHSO_4.H_2O$, $Fe(HSO_4)_3$, sulfamic acid/ultrasound, $HClO_4/SiO_2$, cyanuric chloride, $K_5CoW_{12}O_{40}.3H_2O$, silica-supported molybdophosphoric acid, copper *p*-toluenesulfonate (*p*-TSA), silica chloride, and hexanesulfonic acid sodium salt.[12] However, the major problems associated with these reactions in most of the published procedures are that high catalyst loading, long reaction times, unsatisfactory yields, harsh reaction conditions, expensive catalysts, and tedious work-up procedure. Therefore, the development of a suitable method using additional reagents and catalysts for the efficient synthesis of 1-amidoalkyl-2-naphthols remains an attractive field to researchers. Recently, solid-supported reagents, such as silica gel–supported acids, have gained considerable interest in organic synthesis because of their unique properties of the reagents such as high efficiency caused by more surface area, more stability and reusability, low toxicity, greater selectivity and ease of handling.[13] In recent years, antimony trichloride has been used as catalyst in many important organic reactions, because this compound not only is commercially available and inexpensive, but also is easier to handle than other metal halides such as $InCl_3$,$GdCl_3$, and $TiCl_4$.[14] In continuation of our work on new synthetic methodologies,[15] we wish to report an efficient method for the synthesis of 1-amidoalkyl-2-naphthols in high yields in the presence $SbCl_3$-SiO_2 as heterogeneous and reusable catalyst under solvent free conditions (Scheme 1).

EXPERIMENTAL

All chemicals were commercially available and used without further purification. All yields refer to isolated products after purification. All the products were characterized by comparison of spectroscopic data (IR, ^{1}H NMR spectra) and melting points with authentic samples. The catalyst was synthesized according to the literature.[16] Melting points were recorded on an electrothermal type 9100 melting point apparatus. 1-amidoalkyl-2-naphthols were prepared according to the following general procedure: A mixture of 2-naphthol **1** (1 mmol), aromatic aldehyde **2a-k** (1 mmol), acetamide **3** (1 mmol), and $SbCl_3$-SiO_2 (0.08 g) was heated on the oil bath at 120°C for 3–8 min. The

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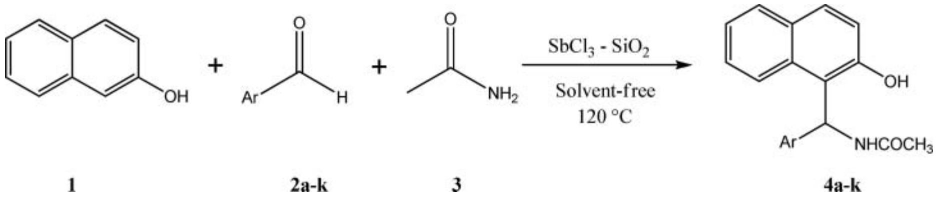

SCH. 1.

reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added. The solid residue was dissolved in ethyl acetate and mixture stirred for 5 min. The catalyst was filtered off and the crude product was collected from the filtrate after evaporation of the solvent and recrystallized from ethanol to give compounds **4a-k** in high yields. All the 1-amidoalkyl-2-naphthols are known and were identified by comparison of their physical and spectroscopic data (IR, NMR) with those of authentic samples.[12]

The spectral data of some representative amidoalkyl naphthols are the following:

N-[(2-Hydroxynaphthalen-1-yl)(4-chlorophenyl)methyl]acetamide (**4c**): IR (KBr, cm^{-1}): 3418, 3316, 3070, 1621, 1595, 1561, 1515, 1467, 1392, 1281, 1201, 1141, 1051, 939, 884, 784, 744, 714. ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 3.16 (s, 3H), 7.09 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.8 Hz, 1H), 7.27–7.31 (m, 3H), 7.38 (brd, 1H), 7.76–7.81 (m, 3H), 8.46 (d, J = 8.1 Hz, 1H), 10.03 (s, 1H). N-[(2-Hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl]acetamide (**4f**): IR (KBr, cm^{-1}): 3391, 3267, 2593, 1648, 1603, 1522, 1438, 1063, 825, 739, 447. ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 2.02 (s, 3H), 7.19 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.28 (t, J = 7.47 Hz, 1H), 7.40 (t, J = 7.34 Hz, 1H), 7.54–7.57 (m, 2H), 7.88 (t, J = 9.38 Hz, 2H), 7.89 (brd, 1H), 8.13 (d, J = 8.0 Hz, 2H), 8.57 (d, J = 8.0 Hz, 1H), 10.11 (s, 1H).

RESULTS AND DISCUSSION

For our investigations, $SbCl_3$-SiO_2 was prepared according to the literature procedure.[16] The synthesis of 1-amidoalkyl-2-naphthols was achieved by the one-pot, three-component condensation of aryl aldehydes, 2-naphthol, and acetamide in the presence of $SbCl_3$-SiO_2 as a heterogeneous catalyst (Scheme 1). To optimize the reaction conditions, the reaction of benzaldehyde (1 mmol), 2-naphthol (1 mmol), and acetamide (1 mmol) in the presence of $SbCl_3$-SiO_2 (0.08 g) was selected as a model. The reaction was carried out in various solvents and under solvent-free conditions. As shown in Table 1, in comparison with conventional methods, the yields of the reaction under solvent-free conditions are greater and the reaction time is shorter. The shortest time and best yield were achieved at 120°C. Next, to find the optimum quantity of $SbCl_3$-SiO_2, the reaction of benzaldehyde, 2-naphthol, and acetamide was carried out under the previously mentioned conditions using different quantities of catalyst at 120°C. The use of 0.08 g of catalyst resulted in the highest yield in 7 min (Table 2).

TABLE 1
Synthesis of 1-amidoalkyl-2-naphthol **4a** in the presence of $SbCl_3$-SiO_2 (0.08 g) in different solvents and optimization of temperature in solvent-free conditions

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)*
1	MeOH	64	300	Trace
2	EtOH	78	300	73
3	CH_3CN	81	300	60
4	H_2O	100	300	63
5	Solvent-free	100	7	80
6	Solvent-free	120	7	91
7	Solvent-free	130	7	91

*The yields were calculated based on benzaldehyde and refer to the pure isolated product.

Thus, we prepared a range of 1-amidoalkyl-2-naphthols under the optimized reaction conditions. In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the expected products in excellent yields and short reaction times. The kind of aldehyde has no significant effect on the reaction. The results are shown in Table 3. It was showed that both electron-rich and electron-deficient aldehydes reacted well, mostly leading to high yields of products.

TABLE 2
Optimization of the amount of catalyst in the preparation of 1-amidoalkyl-2-naphthol **4a***

Entry	Catalyst (g)	Time (min)	Yield (%)**
1	None	120	No reaction
2	0.03	7	60
3	0.05	7	81
4	0.08	7	91
5	0.09	7	92
6	0.1	7	92

*1 mmol 2-naphthol, 1 mmol acetamide, and 1 mmol benzaldehyde at 120°C. **The yields were calculated based on benzaldehyde and refer to the pure isolated product.

TABLE 3
Preparation of 1-amidoalkyl-2-naphthols using $SbCl_3$-SiO_2 (0.08g) as catalyst*

Entry	Ar	Time/min	Product	Yield**/%	m.p. (Lit. m.p)/°C (12)
1	Phenyl	7	**4a**	91	241–243 (245–246)
2	4-Br-phenyl	6	**4b**	89	226–229 (227–229)
3	4-Cl-phenyl	5	**4c**	90	224–226 (224–227)
4	2-NO_2-phenyl	3	**4d**	90	179–181 (180–182)
5	3-NO_2-phenyl	4	**4e**	92	235–237 (236–237)
6	4-NO_2-phenyl	3	**4f**	90	246–248 (248–250)
7	4-OMe-phenyl	8	**4g**	89	183–185 (184–186)
8	4-Me-phenyl	5	**4h**	90	221–223 (222–223)
9	4-F-phenyl	6	**4i**	88	201–203 (203–205)
10	2-Cl-phenyl	8	**4j**	85	196–198 (194–196)
11	2,4-Cl_2-phenyl	4	**4k**	90	196–198 (198–199)

*1 mmol 2-naphthol, 1 mmol acetamide, and 1 mmol aryl aldehyde at 120°C under solvent-free conditions. **The yields were calculated based on aryl aldehyde and refer to the pure isolated products.

The recyclability of the catalyst in the reaction of benzaldehyde (10 mmol), 2-naphthol (10 mmol), and acetamide (10 mmol) in the presence of $SbCl_3$-SiO_2 (0.8 g) was also checked. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added. The solid residue was dissolved in ethyl acetate and mixture stirred for 5 min. The catalyst was separated by simple filtration, dried at 100°C under vacuum for 2 h and reused for the similar

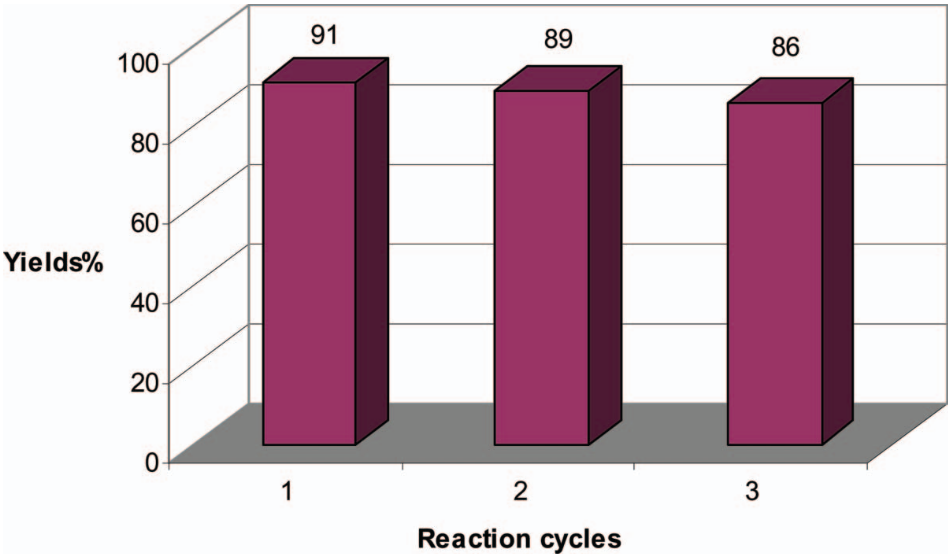

FIG. 1. Recycling experiment for $SbCl_3$-SiO_2 (color figure available online).

TABLE 4

Comparison results of $SbCl_3$-SiO_2 with other catalysts reported in the literature*

Entry	Condition	Catalyst	Time/min	Yield%
1	Under reflux	$Ce(SO_4)_2$	2160	72
2	Solvent-free, 125°C	Montmorillonite K-10 clay	90	89
3	Solvent-free, 125°C	Iodine	330	85
4	Solvent-free, 125°C	$K_5CoW_{12}O_{40} - 3H_2O$	120	90
5	Solvent-free, 125°C	*p*-TSA	300	88
6	Solvent-free, 110°C	Cation-exchanged resins	20	81
7	Solvent-free, 125°C	$HClO_4$- SiO_2	40	89
8	Solvent-free, 120°C	$SbCl_3$-SiO_2	7	91

*Based on 1 mmol 2-naphthol, 1 mmol acetamide, and 1 mmol benzaldehyde.

reaction. As it is shown in Figure 1, the catalyst could be reused at least three times without significant loss of activity.

To show the merit of the present work in comparison with reported results in the literature, we compared reactions of $SbCl_3$-SiO_2 with $Ce(SO_4)_2$, montmorillonite K-10 clay, iodine, $K_5CoW_{12}O_{40}$, $3H_2O$, copper *p*-toluenesulfonate (*p*-TSA), cation-exchanged resins, and $HClO_4$-SiO_2 (12) in the synthesis of 1-amidomethyl-2-naphthol derivatives. As shown in Table 4, $SbCl_3$-SiO_2 can act as high-efficiency catalyst with fast time and high yields of the obtained products.

CONCLUSION

In conclusion, we report on a new simple catalytic method for the synthesis of 1-amidoalkyl-2-naphthols by one-pot condensation reaction of 2-naphthols, acetamide, and aryl aldehydes using $SbCl_3$-SiO_2 as an efficient, reusable, and green heterogeneous catalyst under solvent-free conditions. The catalyst could be recycled after a simple work-up, and reused at least three runs without appreciable reduction in its catalytic activity. High yields, short reaction times, easy work-up, and absence of any volatile and hazardous organic solvents are some advantages of this protocol.

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