Application of nano SnO₂ as a green and recyclable catalyst for the synthesis of 2-aryl or alkylbenzoxazole derivatives under ambient temperature

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Abstract. Application of nano SnO₂ as an efficient and benign catalyst has been explored for the synthesis of 2-aryl or alkylbenzoxazole derivatives via condensation reaction of aldehyde with 2-aminophenol. The reactions proceed under heterogeneous and mild conditions in ethanol at room temperature to provide 2-aryl or alkylbenzoxazoles in high yields.

Keywords. Nano-catalyst; benzoxazole; morphological characterization; nano SnO₂.

1. Introduction

Nanoscience and nanotechnology in the last decade, have turned into an admired field for research and development. Today, nanotechnology plays an important role in industries and business.¹ Due to the chemical and physical properties nanoscale materials in comparison to the macro and micro systems, they have opened up a new vision in application fields including optoelectronics, sensing, medicine and catalysis.^{2,3} Chemists have made considerable achievements in heterogeneous catalysis,⁴ and homogeneous catalysis.^{5–8} Heterogeneous catalysis, that benefits from easy removal of catalyst materials and possible use at high temperatures, suffered for a long time from lack of selectivity and understanding of the mechanistic aspects that are indispensable in parameter improvements.

Transition-metal nanoparticles (NPs) are materials: containing a few tens to several thousand metal atoms, which are stabilized by ligands, polymers or dendrimers as protecting agents for their surfaces. Among the different kind of metal oxide NPs, SnO₂ showed great promise. As a stable and *n*-type large band gap semiconductor, SnO₂ has excellent electrical and optical properties such as low resistivity, peculiar optical transparency and high theoretical specific capacity.⁹ It has been generally used as heat mirrors, gas sensors, photocatalysts, glass coatings, transparent

electrodes for solar cells and storage applications.^{9,10} One-dimensional (1D) nanomaterials of SnO₂ have been found to demonstrate peculiar chemical and optoelectronic properties due to their direct channels for efficient electron transport.^{11–15}

There has been a recent expansion of a class of new benzoxazole syntheses because of their occurrence in a number of natural products,^{16–18} and their potential use as cytotoxic agents,^{19–21} selective peroxisome proliferator-activated receptor antagonists,²² cathepsin S inhibitors,²³ anticancer agents,²⁴ estrogen receptor agonists,²⁵ HIV reverse transcriptase inhibitors,²⁶ and orexin-1 receptor antagonists.²⁷ They have also found application as herbicides and as fluorescent-whitening agent dyes.²⁸ The methods which have been used to provide access to benzoxazoles include conventional thermal- or microwave-accelerated condensation of 2-aminophenols with carboxylic acid derivatives under metal-catalysed cyclization of 2-halo N-acylanilines,^{29–31} strongly acidic conditions^{32–34} and oxidative cyclization of the Schiff bases derived from 2-aminophenols and aldehydes using oxidants such as pyridinium chlorochromate (PCC),³⁵ PhI(OAc)₂,³⁶ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),³⁷ Ba(MnO₄)₂,³⁸ NiO₂³⁹ and Pd(OAc)₂.⁴⁰

In recent years, many heterogeneous organic reactions have been performed using various reagents supported on solid materials.^{41–43} Such procedures have many advantages over unsupported reagents such as cleaner reactions, easier work-up, less reaction

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time, high yields, and are environmentally benign. In continuation of our studies on developing safe and environmentally benign methodologies for organic synthesis, herein, we report for the first time the synthesis of 2-aryl or alkylbenzoxazole derivatives using nano tin dioxide as a catalyst and employing ethanol as solvent at room temperature.

2. Experimental

2.1 General procedure for the synthesis of 2-aryl or alkylbenzoxazoles catalysed by nano SnO_2

To a mixture of aromatic aldehyde (1 mmol) and 2-aminophenol (1 mmol) (synthesis of 2-arylbenzo[d]oxazole), or orthoester (1 mmol) and 2-aminophenol (1 mmol) (synthesis of 2-alkylbenzo[d]oxazole) dissolved in ethanol (3 ml) was added SnO_2 (1 mol%). The resulting mixture was stirred at room temperature for

an appropriate time. After completion of the reaction as monitored by TLC (*n*-hexan/ethyl acetate 5:2), the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether (3 ml) and heated at 30°C for 5 min. The mixture was then cooled to room temperature and filtered to remove the catalyst. The filtrate was evaporated under reduced pressure to isolate a solid residue which was recrystallized from ethanol–water (10:1) to afford pure products. The physical data (M.p, IR, NMR) of these known compounds were found to be identical with those reported in the literature.

2.2 Spectral data for the synthesis of 2-aryl or alkylbenzoxazole derivatives

2.2a 2-(4-Chlorophenyl)benzo[d]oxazole (table 1, entry 11): Yield: 95%; M.p. 143–145°C (ref. 33, 147°C); IR (KBr, cm^{-1}): 3301, 2997, 1621, 1579,

Table 1. Synthesis of 2-arylbenzoxazole derivatives using nano SnO_2 as a catalyst.^a

Entry	R	Aminophenol	M.p (°C)	Time (min)	Yield (%) ^b [Ref.] ^c
1	H	2a	103–105	21	90 ⁴⁴
2	2-OH	2a	118–120	20	90 ⁴⁵
3	2-OMe	2a	55–57	18	90 ⁴⁶
4	3-OMe	2a	72–74	15	92 ⁴⁷
5	4-OMe	2a	98–100	12	94 ⁴⁴
6	2-Me	2a	65–67	15	90 ⁴⁸
7	4-Me	2a	113–115	13	94 ⁴⁴
8	2,5- <i>t</i> .Bu-4-OH	2a	170–172	20	90 ⁴⁹
9	2-Cl	2a	71–73	15	91 ⁵⁰
10	3-Cl	2a	134–136	12	93 ⁵⁰
11	4-Cl	2a	143–145	10	95 ³³
12	4-F	2a	103–105	10	95 ⁵¹
13	4-Br	2a	161–163	12	94 ⁵²
14	4-CO ₂ Me	2a	200–202	7	97 ⁵³
15	4-CN	2a	85–87	7	97 ⁵⁴
16	4-NO ₂	2a	265–267	5	98 ³³
17	2-Furyl	2a	83–85	15	94 ⁴⁴
18	2-Thienyl	2a	105–107	18	94 ⁴⁴
19	2-OH	2b	135–137	18	92 ⁵⁵
20	5-Br-2-OH	2b	168–170	20	91 ⁵⁶
21	2,5- <i>t</i> .Bu-4-OH	2b	167–169	20	91 ⁴⁹
22	H	2c	103–105	17	93 ⁵⁰
23	2-OH	2c	147–149	15	91 ⁵⁵
24	5-Br-2-OH	2c	173–175	18	93 ⁵⁶
25	2,5- <i>t</i> .Bu-4-OH	2c	196–198	18	92 ⁴⁹
26	H	2d	163–165	13	94 ⁴⁸
27	2,5- <i>t</i> .Bu-4-OH	2d	176–178	15	94 ⁴⁹

^aProducts were identified by comparison of their physical and spectral data with those of authentic samples

^bIsolated yields

^cReferences for known compounds

Table 2. Synthesis of 2-alkylbenzoxazole derivatives catalysed by nano SnO₂.^a

Entry	Orthoester	Aminophenol	M.p (°C)	Time (min)	Yield (%) ^b [Ref.] ^c
1	HC(OMe) ₃	2a	99–101	35	91 ³⁶
2	MeC(OMe) ₃	2a	113–115	30	93 ³⁶
3	EtC(OEt) ₃	2a	28–30	25	93 ⁵⁷
4	HC(OMe) ₃	2b	101–103	27	93 ³⁶
5	MeC(OMe) ₃	2b	85–87	21	94 ⁵⁸
6	EtC(OEt) ₃	2b	32–34	18	95 ⁵⁸
7	HC(OMe) ₃	2c	38–40	20	93 ⁵⁹
8	MeC(OMe) ₃	2c	53–55	15	95 ⁵⁸
9	EtC(OEt) ₃	2c	58–60	12	96 ⁵⁸

^aProducts were identified by comparison of their physical and spectral data with those of authentic samples

^bIsolated yields

^cReferences for known compounds

1481, 1376, 1238, 1195, 748; ¹H NMR (400 MHz, DMSO-*d*₆, δ ppm): 7.90 (d, 2H, J = 8.7 Hz), 7.50 (d, 2H, J = 8.6 Hz), 7.33 (d, 1H, J = 7.8 Hz), 7.26 (t, 1H, J = 7.7 Hz), 7.06 (d, 1H, J = 7.9 Hz), 6.96 (t, 1H, J = 7.8 Hz); ¹³C-NMR (100 MHz, DMSO-*d*₆, δ ppm): 155.5, 152.4, 137.7, 135.2, 134.3, 129.9, 129.3, 129.2, 120.2, 115.8, 115.2.

2.2b 2-(4-Nitorophenyl)benzo[*d*]oxazole (table 1, entry 16): Yield: 98%; M.p. 265–267°C (Ref. 33, 266–268°C); IR (KBr, cm⁻¹): 3324, 2957, 1587, 1515, 1342, 1236, 1193, 838; ¹H NMR (400 MHz, DMSO-*d*₆, δ ppm): 8.37 (d, 2H, J = 8.7 Hz), 8.11 (d, 2H, J = 8.6 Hz), 7.39 (d, 1H, J = 7.8 Hz), 7.31 (t, 1H, J = 7.8 Hz), 7.08 (d, 1H, J = 7.9 Hz), 6.98 (t, 1H, J = 7.7 Hz); ¹³C-NMR (100 MHz, DMSO-*d*₆, δ ppm): 153.8, 152.9, 149.3, 141.1, 134.5, 130.4, 129.3, 124.1, 120.4, 115.9, 115.6.

2.2c Benzo[*d*]oxazole (table 2, entry 1): Yield: 91%; M.p. 99–101 (Ref. 36, 102°C); IR (KBr, cm⁻¹): 3055, 2956, 1575, 1459, 1376, 955, 879; ¹H NMR (400 MHz, DMSO-*d*₆, δ ppm): 8.84 (s, 1H), 7.41 (t, 1H, J = 6.7 Hz), 7.33 (t, 1H, J = 6.9 Hz), 7.28 (d,

J = 6.8 Hz, 1H), 7.25 (d, J = 6.7 Hz, 2H); ¹³C-NMR (100 MHz, DMSO-*d*₆, δ ppm): 146.3, 131.2, 131.1, 130.1, 129.5, 129.2, 127.7.

3. Results and discussion

First, we report a very simple method for the synthesis of 2-arylbenzoxazole derivatives (**3**) by condensation of aromatic aldehydes (**1**) with 2-aminophenol (**2**) under heterogeneous and mild reaction conditions, catalysed by SnO₂ nano-catalyst at room temperature (scheme 1).

To study the generality of this process, several examples illustrating this method for the synthesis of 2-arylbenzoxazole derivatives were studied. To show the general applicability of this method, various aromatic aldehydes were efficiently reacted with one equivalent of 2-aminophenol in the same conditions. These results encouraged us to investigate the scope and the generality of this new protocol for various aromatic aldehydes under optimized conditions. As shown in table 1, a series of aromatic aldehydes underwent electrophilic substitution reaction with 2-aminophenol to afford a wide range of 2-arylbenzoxazole derivatives in good to excellent yields without any side products. The

Scheme 1. Synthesis of 2-arylbenzoxazole derivatives using nano SnO₂ as a catalyst.

Scheme 2. Synthesis of 2-alkylbenzoxazole derivatives catalysed by nano SnO₂.

nature and electronic properties of the substituents on the aromatic ring, affect the conversion rate, and aromatic aldehydes having electron-withdrawing groups on the aromatic ring (table 1, entries 14–16) react faster than electron-donating groups (table 1, entries 5, 7, 19 and 23). Though para- and meta-substituted aromatic aldehydes gave good results, ortho-substituted aromatic aldehydes (such as table 1, entries 2, 6, 9, 19 and 23) gave lower yields because of the steric effects.

Also, we studied an efficient and simple procedure for the condensation reaction of 2-alkylbenzoxazole derivatives (5) at room temperature using SnO₂ as catalyst (scheme 2). The reaction of 2-aminophenol (2) with 1 mmol of orthoester (4) in ethanol in the presence of SnO₂ furnished the desired fused 2-alkylbenzoxazole derivatives in less reaction times and high yields.

After optimizing the reaction conditions, the investigation was continued by performing the reaction between 2-aminophenol with orthoester. To show the general applicability of this method, various orthoesters were efficiently reacted with one equivalent of 2-aminophenol in the same condition. These results encouraged us to investigate the scope and the generality of this new protocol for various orthoesters under optimized conditions. As shown in table 2, trialkyl orthoacetates and trialkyl orthopropionates with

2-aminophenols at room temperature react faster than trialkyl orthoformates with 2-aminophenols.

To achieve the best results in terms of yield and reaction time, we examined the efficiency of different reaction media and catalyst amounts in condensation reaction of benzaldehyde with 2-aminophenol (synthesis of 2-phenylbenzo[d]oxazole) and reaction of trimethyl orthoacetate with 2-aminophenol (synthesis of 2-methylbenzo[d]oxazole) as a model reaction. As shown in table 3, a significant enhancement of the reaction rate and improvement of the yield of the reaction were observed when 1 mol% of SnO₂ in ethanol was used (entry 2). In the absence of SnO₂ catalyst, no formation of the expected product was detected even after 2 h (entry 7). In order to evaluate the effect of the catalyst concentration, the reaction was also conducted in the presence of various amounts of catalyst (2, 5 and 10 mol%) at room temperature (entries 8, 9 and 10). Also, from table 3, we know that ethanol is obviously the best choice for these reactions.

In an attempt to observe the efficiency of the recycled catalyst in these reactions, the reaction of benzaldehyde with 2-aminophenol (synthesis of 2-phenylbenzo[d]oxazole) and reaction of trimethyl orthoacetate with 2-aminophenol (synthesis of 2-methylbenzo[d]oxazole) were performed in the

Table 3. Solvent effect in the synthesis of benzoxazole derivatives catalysed by nano SnO₂.

Entry	Solvent	Catalyst amount	2-Phenylbenzo[d]oxazole ^a		2-Methylbenzo[d]oxazole ^b	
			Time (min)	Yield (%) ^c	Time (min)	Yield (%) ^c
1	H ₂ O	1 mol%	75	51	90	38
2	C ₂ H ₅ OH	1 mol%	21	90	30	93
3	CH ₃ CN	1 mol%	25	90	40	93
4	THF	1 mol%	35	87	45	90
5	Toluene	1 mol%	50	85	60	85
6	Benzene	1 mol%	60	81	75	78
7	C ₂ H ₅ OH	–	120	–	120	–
8	C ₂ H ₅ OH	2 mol%	21	90	30	92
9	C ₂ H ₅ OH	5 mol%	21	89	30	92
10	C ₂ H ₅ OH	10 mol%	25	87	40	90

Reaction condition: ^a2-Aminophenol (1 mmol), benzaldehyde (1 mmol), solvent (2 mL)

^b2-Aminophenol (1 mmol), trimethyl orthoacetate (1 mmol), solvent (2 mL)

^cIsolated yield

Table 4. Investigation of reusability of nano SnO₂ catalyst in the synthesis of benzoxazole derivatives.

Run number	Isolated yield ^a	
	2-(4-Nitrophenyl)benzo[d]oxazole ^b	2-Methylbenzo[d]oxazole ^c
Fresh	98	93
1	97	93
2	96	91
3	96	91
4	93	89

Reaction condition: ^aIsolated yield^b2-Aminophenol (1 mmol), 4-nitrobenzaldehyde (1 mmol), SnO₂ nano catalyst (1 mol%), ethanol solvent (2 mL)^c2-Aminophenol (1 mmol), trimethyl orthoacetate (1 mmol), SnO₂ nano catalyst (1 mol%), ethanol solvent (2 mL)

presence of fresh SnO₂ catalyst (1 mol%) at room temperature (table 4). The recovered catalyst in this reaction work-up was reused in subsequent reactions and found to be almost as reactive as the fresh catalyst without significant loss in the catalytic activity.

The morphology, crystal structure and sizes of the SnO₂ nano-catalyst in different synthetic stage are characterized by X-ray diffraction, and transmission electron microscopy (TEM). The powder X-ray diffraction pattern of reaction media (SnO₂ nano-catalyst in pure form) (figure 1) was recorded on a Rigaku D/Max-2200 model diffractometer equipped with horizontal goniometer in $\theta/2\theta$ geometry. The copper K α ($\lambda = 1.5418 \text{ \AA}$) radiation was used and the sample was scanned between 3–80 degrees 2θ . Sharp peaks in the

diffractogram indicate that the reaction media (SnO₂ nano-catalyst in pure form) contain crystalline species. There are several major peaks with 2θ values of 26.6, 33.9, 37.9, 42.6, 51.8, 54.7 and 57.8, corresponding to SnO₂ crystal planes of (1 0 1), (1 1 0), (1 1 1), (2 1 0), (2 1 1), (2 2 0), (0 0 2), respectively. All reflections of SnO₂ NPs are in excellent accordance with a tetragonal rutile structure (JCPDS 41-1445).

TEM images of the SnO₂ nanocatalyst, presented in reaction mixture (nano SnO₂ in the 2-(4-nitrophenyl)benzo[d]oxazole) in different resolution (50, 100, 150, 200 and 300 nm) is shown in figure 2. Obtained pictures showed that the NPs are in good dispersion state. Also, a few quantity of aggregates were observed. The NPs are in the range of 70–120 nm.

Figure 1. XRD diffraction patterns of reaction media (SnO₂ nano-catalyst in pure form).

Figure 2. TEM images of reaction mixture (nano SnO_2 in the 2-(4-nitrophenyl)benzo[d]oxazole) in (a, b) 50, (c,d) 100, (e,f) 150, (g) 200 and (h) 300 nm.

4. Conclusion

In summary, we have demonstrated that SnO_2 nano catalyst is a reusable, cheap and eco-friendly catalyst for the synthesis of 2-aryl or alkylbenzoxazole derivatives. The catalyst offers several advantages including mild reaction conditions, cleaner reactions, high yield of the products, lower catalytic loading and shorter reaction times as well as simple experimental and isolation procedures. Also, the catalyst could be reused easily five times in experiments with a small decrease in the catalytic activity of the recovered catalyst.

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