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Research Article

$NaHSO_4$-SiO_2-Promoted Solvent-Free Synthesis of Benzoxazoles, Benzimidazoles, and Benzothiazole Derivatives

K. Ravi Kumar,[1] P. V. V. Satyanarayana,[2] and B. Srinivasa Reddy[1]

[1] *Research and Development Division, RA Chem Pharma Limited, Prasanth Nagar, Hyderabad 500072, India*
[2] *Department of Chemistry, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur 522510, India*

Correspondence should be addressed to P. V. V. Satyanarayana; chemperuri@yahoo.co.in

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An efficient protocol has been developed for the preparation of a library of benzoxazole, benzimidazole, and benzothiazole derivatives from reactions of acyl chlorides with *o*-substituted aminoaromatics in the presence of catalytic amount of silica-supported sodium hydrogen sulphate under solvent-free conditions. Simple workup procedure, high yield, easy availability, reusability, and use of ecofriendly catalyst are some of the striking features of the present protocol.

1. Introduction

Molecules with benzoxazole, benzimidazole, and benzothiazoles moieties are attractive targets for synthesis since they often exhibit diverse and important biological properties. These heterocycles have shown different pharmacological activities such as antibiotic [1], antifungal [2], antiviral [3], anticancer [4], antimicrobial [5], and anti-Parkinson [6] properties. They have also been used as ligands for asymmetric transformations [7]. Benzimidazole derivatives are a unique and broad spectrum class of antirhino/enteroviral agents such as antiulcerative [8] and antiallergic [9]; they are effective against the human cytomegalovirus [10] and are also efficient selective neuropeptide Y Y1 receptor antagonists [11].

A number of methods are reported for the synthesis of these heterocycles by using different catalysts such as Pd-catalyzed oxidative cyclization [12], ionic liquid-mediated synthesis [13], base-assisted reaction of 1,1-dibromoethanes [14], SiO_2-$ZnCl_2$ [15], $ZrOCl_2{\cdot}8H_2O$ [16], $In(OTf)_3$ [17], polyethylene-glycol-mediated catalysts [18], and different heteropolyacid catalysts [19], which include condensation of orthoesters [20–22], nitriles [23], aldehydes [24–27], carboxylic acids [28–32], acid chlorides [33], amides [34] and esters [35] with *o*-substituted aminoaromatics in the presence of different acids and catalysts. Beckmann rearrangement of *o*-acylphenol oximes [36], photocyclization of phenolic Schiff bases [37], and benzimidazole, synthesis in solvent-free conditions [38] were also used. More recently benzoxazole, benzimidazole, and benzothiozoles were prepared from condensation of aldehydes with *o*-substituted aminoaromatics in the presence of Indion 190 resin [39]. However, many of these methods suffer from one or more of the drawbacks such as requirement of strong acidic conditions, long reaction times, low yields, tedious workup procedures, requirement of excess amounts of reagents, and use of toxic reagents, catalysts or solvents. Therefore, there is a strong demand for a highly efficient and environmentally benign method for the synthesis of these heterocycles.

In recent years, heterogeneous catalysts [40–42] have gained importance in several organic transformations due to their interesting reactivity as well as for economic and environmental reasons. In continuation of our work to develop new methodologies for organic transformations [43–46], we observed that silica-supported sodium hydrogen sulphate is highly efficient catalyst for the synthesis of substituted benzoxazole, benzimidazole, and benzothiazole derivatives through the reaction of *o*-substitued aminoaromatics with different acyl chlorides under solvent-free conditions. The catalyst $NaHSO_4$-SiO_2 can easily be prepared [47] from the readily available $NaHSO_4$ and silica gel (230–400 mesh) and these are inexpensive and nontoxic. Besides, as the reaction

Table 1: Preparation of 2-phenyl benzimidazole using various solvents and temperaures[a].

Entry	Solvent	Time/Temp (°C)	Yield (%)[b]
1	Ethanol	12 hr/80°C	90
2	1,4-Dioxane	12 hr/100°C	80
3	Toluene	12 hr/100°C	72
4	Solvent-free	12 hr/100°C	92
5	Solvent-free	16 hr/100°C	91
6	Solvent-free	08 hr/100°C	82
7	Solvent-free	12 hr/70°C	68

[a]Reaction conditions: *o*-phenylenediamine (1 mmol), benzoyl chloride (1 mmol),$NaHSO_4$-SiO_2 (25%/wt) were stirred in solvent (3 mL) or neat, the temperature and time indicated in Table 1, [b]isolated yields.

is heterogeneous in nature, the catalyst can easily be removed by simple filtration (Scheme 1).

2. Results and Discussions

In order to find the optimum reaction conditions for the condensation reaction, preliminary efforts were mainly focused on the evaluation of different solvents. The model reaction has been carried out between *o*-phenylenediamine and benzoyl chloride in the presence of $NaHSO_4$-SiO_2 catalyst under different solvents and at different temperatures, and results are shown in Table 1.

The effect of solvent, reaction temperature, and time on the reaction was systematically investigated, and the results were summarized in Table 1. The optimized reaction conditions for the reaction were found to be $NaHSO_4$-SiO_2 under solvent-free condition for 12 hr at the temperature of 100°C. Thus, we used $NaHSO_4$-SiO_2 as a catalyst in the present work. In order to elucidate the role of $NaHSO_4$-SiO_2 as catalyst, a controlled reaction was conducted using *o*-phenylenediamine and benzoyl chloride under solvent-free condition in the absence of catalyst. This resulted in the formation of only 7% of the fused product after 12 hr at 100°C. However, reaction with same substrate using 25%/wt of $NaHSO_4$-SiO_2 at 100°C for 12 hr afforded the product in quantitative yield. Lower temperatures required more time for the completion of the reaction and obtained low yields compared to the optimized reaction condition.

As shown in Table 2, different acyl chlorides reacted with different *o*-substituted aminoaromatics without any significant difference in the reaction time to give the corresponding 2-substituted benzoxazole, benzimidazole, and benzothiazole derivatives in good yield. The method has the ability to tolerate other functional groups such as methoxy, methyl, and halides. The products were synthesized in good to excellent yields and characterized by ^{1}H NMR, LCMS, and physical constant. Physical and spectral data of known compounds are in agreement with those reported in literature [48–57].

The reusability of catalyst is important for the large-scale operation and industrial point of view. Therefore, the recovery and reusability of $NaHSO_4$-SiO_2 was examined. The catalyst was separated and reused after washing with EtOAc and drying at 100°C. The reusability of catalyst was investigated in the reaction of *o*-phenylenediamine with benzoyl chloride (Figure 3). The results illustrated in Figure 3 showed that the catalyst can be used four times with consistent yield.

3. Conclusion

In conclusion, $NaHSO_4$-SiO_2 was found to be an efficient catalyst for the formation of benzoxazole, benzimidazole, and benzothiazole derivatives. The use of this inexpensive, easily available, and reusable catalyst makes this protocol practical, environment friendly, and economically attractive. The simple workup procedure, high yields of products, and nontoxic nature of the catalyst are other advantages of the present method.

4. Experimental Section

All ^{1}H NMR spectra were recorded on 400 MHz Varian FT-NMR spectrometers. All chemical shifts are given as δ value with reference to Tetra methyl silane (TMS) as an internal standard. Melting points were taken in open capillaries. The IR spectra were recorded on a PerkinElmer 257 spectrometer using KBr discs. Products were purified by flash chromatography on 100–200 mesh silica gel. The chemicals and solvents were purchased from commercial suppliers either from Aldrich, Spectrochem, and they were used without purification prior to use.

5. FT-IR Spectrum of $NaHSO_4$-SiO_2

The FT-IR spectrum of the catalyst is shown in Figure 1. The catalyst is solid, and its solid-state IR spectrum was recorded using the KBr-disc technique. For silica (SiO_2), the major peaks are broad antisymmetric Si-O-Si stretching from 1000–1100 cm^{-1} and symmetric Si-O-Si stretching near 798 cm^{-1}, and bending modes of Si-O-Si lie around 467 cm^{-1}. The spectrum also shows a broad Si-OH stretching absorption from 3300 to 3500 cm^{-1}.

6. X-Ray Diffraction (XRD) Spectrum of $NaHSO_4$-SiO_2

Powder X-ray diffraction measurement was performed using D8 advance diffractometer. The strongest peaks of XRD pattern correspond to the SiO_2 plane with the other peaks indexed as the [22, 23, 32] planes of supported sodium hydrogen sulphate (Figure 2).

7. General Experimental Procedure

A mixture of 2-amino phenols or *o*-phenylenediamines (1 mmol) and acyl chloride (1 mmol) were place in a sealed vessel containing $NaHSO_4$-SiO_2 (25%/wt) the reaction mixture was stirred at 100°C for 12 hrs. The progress of the

Table 2: Synthesis of 2-substituted benzoxazoles, benzimidazoles, and benzothiazoles[a].

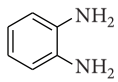
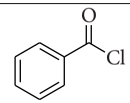
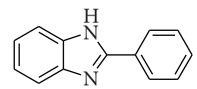
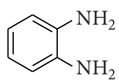
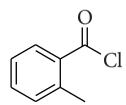
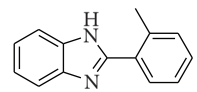
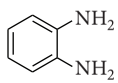
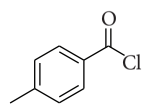
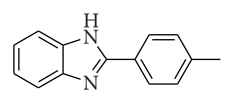
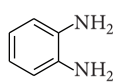
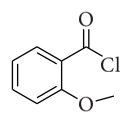
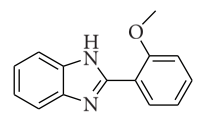
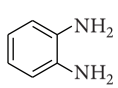
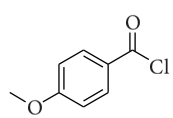
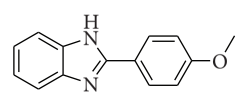
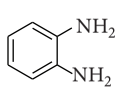
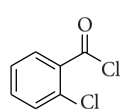
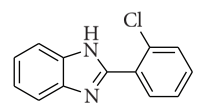
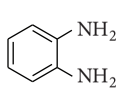
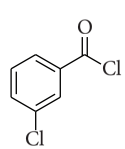
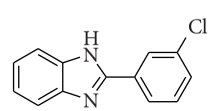
Entry	Amines	Acid chlorides	Product	Yield (%)[b]	M.P. (°C) reported (lit)	M.P. (°C) found[c]
1				92	285–287[48]	289–291
2				87	222–223[48]	220–222
3				93	266–268[48]	265–267
4				86	175–176[50]	173–175
5				91	220–221[48]	218–221
6				88	230–232[49]	231–233
7				87	236–238[49]	234–236

Table 2: Continued.

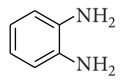
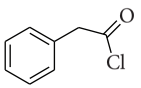
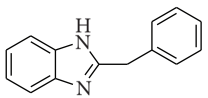
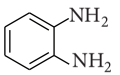
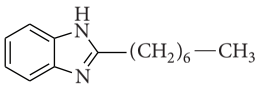
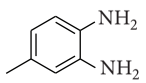
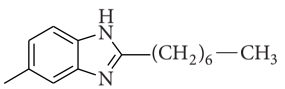
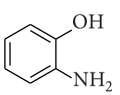
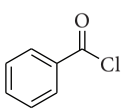
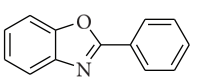
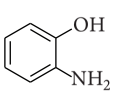
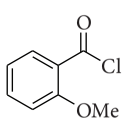
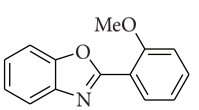
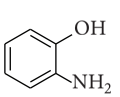
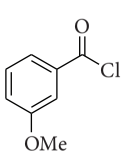
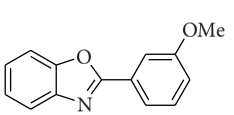
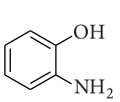
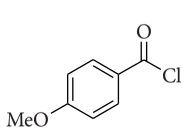
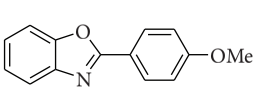
Entry	Amines	Acid chlorides	Product	Yield (%)[b]	M.P. (°C) reported (lit)	M.P. (°C) found[c]
8				90	179–180[48]	177–179
9		$CH_3—(CH_2)_6—COCl$		89	—	146–147
10		$CH_3—(CH_2)_6—COCl$		88	—	88–89
11				93	101–102[51]	102–104
12				83	53–54[52]	54–56
13				87	72–74[53]	70–73
14				89	98–99[51]	97–99

Table 2: Continued.

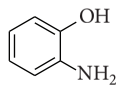
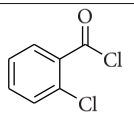
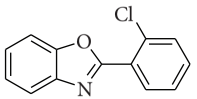
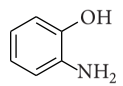
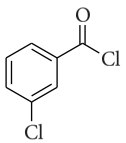
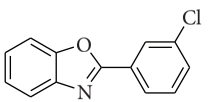
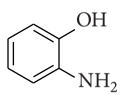
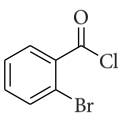
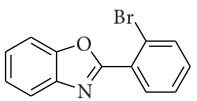
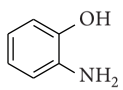
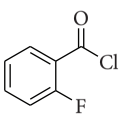
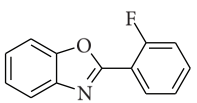
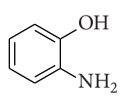
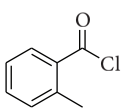
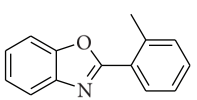
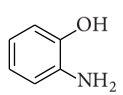
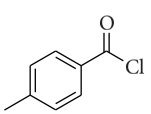
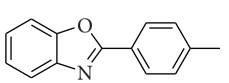
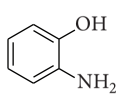
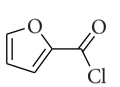
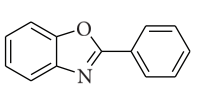
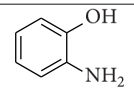
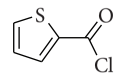
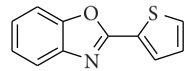
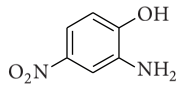
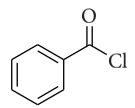
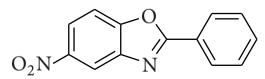
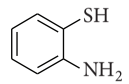
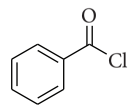
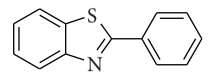
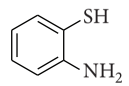
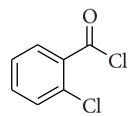
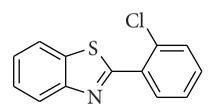
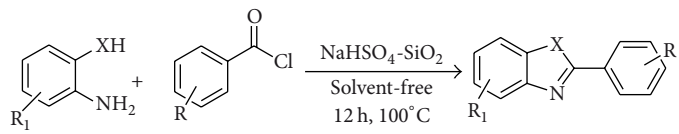
Entry	Amines	Acid chlorides	Product	Yield (%)[b]	M.P. (°C) reported (lit)	M.P. (°C) found[c]
15				81	70–72[54]	70–73
16				86	131–132[54]	131–133
17				84	54–55[52]	53–56
18				83	93–95[53]	92–94
19				85	64–65[55]	63–66
20				94	110–111[51]	114–116
21				93	84–86[51]	85–87

Table 2: Continued.

Entry	Amines	Acid chlorides	Product	Yield (%)[b]	M.P. (°C) reported (lit)	M.P. (°C) found[c]
22				95	104–105[51]	104–107
23				71	165–168[54]	166–169
24				89	107–110[56]	108–110
25				86	71–73[57]	70–72

[a] Reaction conditions: *o*-phenylenediamine (1 mmol), benzoyl chloride (1 mmol), and $NaHSO_4$-SiO_2 (25%/wt) were stirred under solvent-free condition at 100°C for 12 h, [b] isolated yields, [c] all products are solids.



R_1 = H, CH_3, NO_2 X = NH, O, S R = CH_3, OCH_3, Cl, Br, F

Scheme 1

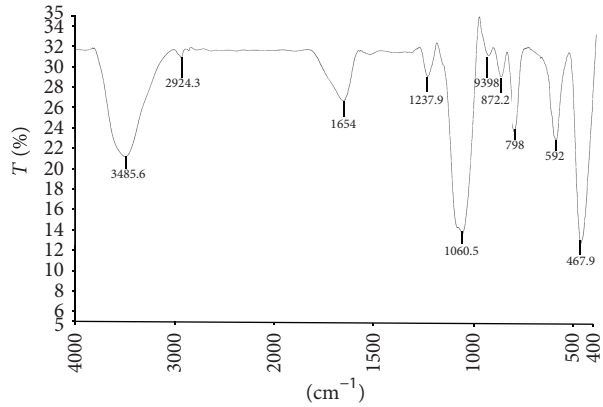


Figure 1: FT-IR spectra of silica-supported sodium hydrogen sulphate.

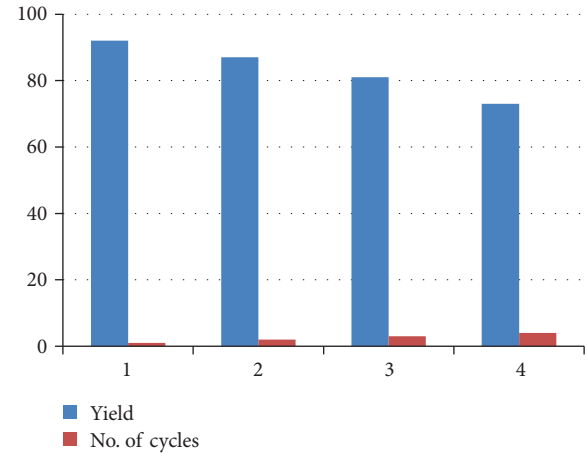


Figure 3: Investigation of reusability of $NaHSO_4$-SiO_2.

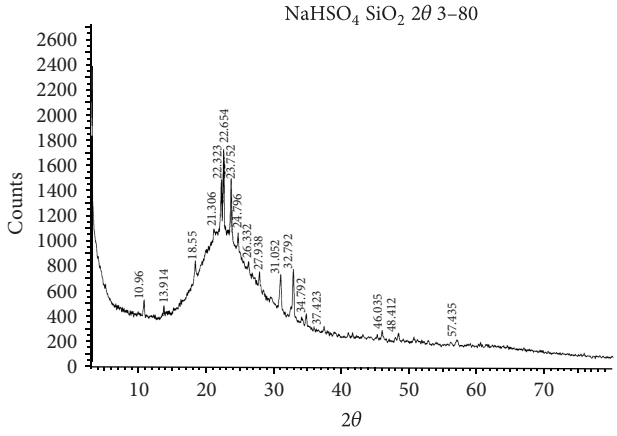


Figure 2: XRD spectra of silica-supported sodium hydrogen sulphate.

reaction was monitored by TLC Hexane: EtOAc (4 : 1) after completion of the reaction, the reaction mixture was cooled and treated by dilution with EtOAc and the catalyst was removed by filtration. Obtained filtrate was evaporated under reduced pressure to get the crude product, which was purified by column chromatography to give 2-substituted benzoxazoles, benzimidazole, and benzothioazole derivatives.

8. Representative Spectral Data

2-Phenyl-1H-benzo [d]Imidazole (Table 2, Entry 1). ^{1}H NMR (DMSO-d_6): δ 13.02 (br s, 1H), 8.20 (d, J = 7.6 Hz, 2H), 7.67–7.65 (m, 1H), 7.56–7.49 (m, 4H), 7.22–7.18 (m, 2H); (LC-MS) *m/z*: 195.08 $[M + H]^+$; IR (KBr, cm^{-1}): 3420, 2920, 2627, 1623, 1410, 1276, 1119, 970, 738. *Anal.* Calcd. For $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.11; H, 5.01; N, 14.38.

2-Heptyl-1H-benzo [d]Imidazole (Table 2, Entry 9). ^{1}H NMR (DMSO-d_6): δ12.11 (br s, 1H), 7.49 (d, J = 8 Hz, 1H), 7.38 (d, J = 6.4 Hz, 1H), 7.09–7.12 (m, 2H), 2.78 (t, J = 7.6 Hz, 2H), 1.77–1.73 (m, 2H), 1.31–1.25 (m, 8H), 0.85 (t, J = 6.4 Hz, 3H); (LC-MS) *m/z*: 217.21 $[M+H]^+$; IR (KBr, cm^{-1}): 3467, 2926, 2683, 1624, 1451, 1272, 1028, 750. *Anal.* Calcd. For $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.70; H, 9.28; N, 12.86.

2-Heptyl-5-methyl-1H-benzo [d]Imidazole (Table 2, Entry 10). ^{1}H NMR (DMSO-d6): δ11.98 (br s, 1H), 7.36–7.18 (m, 2H), 6.93-6.89 (m, 1H), 2.74 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.78–1.70 (m, 2H), 1.30–1.21 (m, 8H), 0.85 (t, J = 6.4 Hz, 3H); (LC-MS) *m/z*: 231.18 [M+H]+; IR (KBr, cm−1): 2946, 2763, 1861, 1448, 1281, 1030, 803. Anal. Calcd. For C15H22N2: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.19; H, 9.58; N, 12.15.

2-Phenyl Benzo [d]Oxazole (Table 2, Entry 11). ^{1}H NMR (CDCl3): δ 8.27–8.24 (m, 2H), 7.79–7.76 (m, 1H), 7.60–7.57 (m, 1H), 7.54–7.51 (m, 3H), 7.38–7.32 (m, 2H); (LC-MS) *m/z*: 196.20 [M+H]+; IR (KBr, cm−1): 3435, 2921, 1615,

1551, 1240, 743. Anal. Calcd. For C13H9NO: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.86; H, 4.61; N, 7.14; O.

2-*Phenyl Benzo [d]Thiazole (Table 2, Entry 24).* ^{1}H NMR (CDCl3): δ8.11–8.07 (m, 3H), 7.91 (d, J = 8.4 Hz, 1H), 7.51-7.40 (m, 4H), 7.39-7.37 (m, 1H); (LC-MS) *m/z:* 212.12 $[M+H]^+$; IR (KBr, cm^{-1}): 3063, 2924, 1686, 1477, 1311, 1223, 961, 766, 685. *Anal.* Calcd. For $C_{13}H_9NS$: C, 73.90; H, 4.29; N, 6.63. Found: C, 73.87; H, 4.27; N, 6.59.

Acknowledgments

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