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Note

A mild, efficient and one-pot synthesis of 2-substituted benzimidazoles by $ZrOCl_2.8H_2O$ catalyzed ring closure reaction

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A mild, efficient and one-pot synthesis of an array of 2-substituted benzimidazoles from an appropriate *o*-phenylenediamine and orthoesters such as orthoformate, orthoacetate and orthovalerate using $ZrOCl_2.8H_2O$, at room temperature and under microwave irradiation is described. Eco-friendly, solvent-free methodology has been employed under microwave condition. Compared with the conventional method, microwave irradiation method has the advantages of excellent yields (81-93%) and shorter reaction time (5-10 min).

Keywords: $ZrOCl_2.8H_2O$, benzimidazole, orthoester, microwave irradiation

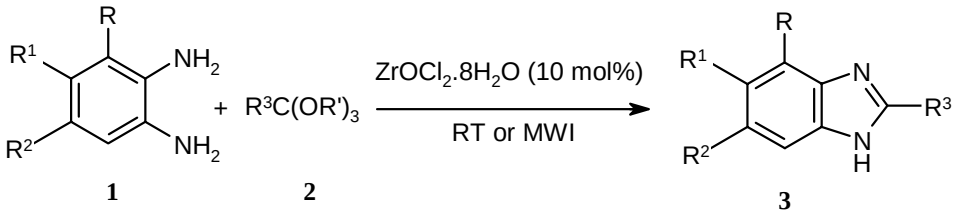
A large number of benzimidazole derivatives exhibit diverse biological and pharmacological activities[1-6]. Benzimidazole-based structures have resulted in marketed medicines such as Omeprazole[7] and Pimobendan[8]. Moreover, several *N*-substituted benzimidazole derivatives also exhibit significant activity against several viruses, including HIV[9], herpes simplex (HSV-1)[10], influenza[11], picorna[12], human cytomegalovirus (HCMV)[9] and hepatitis C virus[13,14]. In recent years benzimidazoles have been reported to act as topoisomerase-I inhibitors[15], selective neuropeptide YY1 receptor antagonists[16], angiotensin-II inhibitors[6], 5-HT_3 antagonists in isolated guinea-pig ileum[17], a treatment for interstitial cystitis[18] and as factor Xa inhibitors[19]. In addition, some benzimidazole derivatives may help to reduce some of the significant toxic side effects produced by the acyclo nucleoside analogs like acyclovir 9-[(2-hydroxyethoxy)methyl]guanine, DHPG [(1,3-dihydroxy propoxy)methyl]guanine[20].

In view of the importance of benzimidazoles, many classical methods for the synthesis of 2-substituted benzimidazoles have been reported in the literature. Usually, phenylenediamine and carboxylic acids or carboxylic acid derivatives[21] are the starting materials for the synthesis of 2-substituted benzimidazoles under vigorous dehydrating conditions[22]. A number of synthetic methodologies have been developed in recent years to provide a variety of new reagents for the synthesis of 2-substituted benzimidazoles. These include, conversion of esters using an aluminium reagent[23], the reaction of *N*-ethoxycarbonylthioamide with 1,2-diamines[24], the reaction of aldehydes with 1,2-diamines followed by *N*-halosuccinamide[25], the reaction of aldehydes with 1,2-diamines in presence of iodine[26], the reaction of *o*-nitroaniline and carboxylic acids in a two step process using zinc[27], iron[28], tin(II)chloride[29], hydrogen[30] or Raney nickel[31] and one pot preparation using $SnCl_2$ (ref. 32). The other systems using *o*-dinitrobenzene[33], azalactone[34], 2-aryl-1,1-dibromomethanes[35], nitriles[36] and acid chlorides[37], as starting materials for this synthesis have also been recommended. However, many of these synthetic protocols suffer from disadvantages, such as requiring rigorous anhydrous conditions[34], use of organic solvents[23-25], harsh reaction conditions[23], prolonged reaction time[25], use of expensive reagents[23] and multi-step procedure[27-31]. Therefore, a rapid and more convenient method for the synthesis of these compounds still remains an active area of research.

As part of the program aimed at developing new selective and environmentally friendly methodologies, particularly C-C and C-X bond formation, it is wished to report herein another remarkable catalyst $ZrOCl_2.8H_2O$ for the synthesis of 2-substituted benzimidazoles. Many advantages such as ready availability, excellent solubility in water, inexpensive, eco-friendly nature, uncomplicated handling, and non-toxicity make $ZrOCl_2.8H_2O$ a potent catalyst in organic synthesis[38].

Results and Discussion

In continuation of the interest on zirconium salt-catalyzed organic reactions[39], herein is described a mild, efficient, one-pot and high yielding protocol for the synthesis of 2-substituted benzimidazoles **3a-r** from *o*-phenylenediamine **1** and orthoesters **2** in the presence of catalytic amount of $ZrOCl_2.8H_2O$ (10 mol%) at RT as well as under solvent-free microwave irradiation conditions (**Scheme I**).



Scheme I

The synthesis of 2-substituted benzimidazoles **3a-r** was carried out by the condensation-cyclization reaction between the appropriate *o*-phenylenediamine **1** and orthoesters **2** in presence of catalytic amount of $ZrOCl_2.8H_2O$ (10 mole%). In the "conventional" method, the reactions were performed in ethyl alcohol (5 mL) at RT over a long period of time (1.5-6.0 hr) and resulted in low yields of isolated products (62-80%). Under similar conditions, formation of products was not observed, even after an extended reaction time (30 hr), in the absence of the catalyst.

Microwave assisted technology has been adopted in order to achieve striking reduction in the reaction time, better yields and cleaner reactions. Under microwave method, a mixture of an appropriate *o*-phenylenediamine **1** and orthoester **2** and a catalytic amount of $ZrOCl_2.8H_2O$ (10 mole%) was irradiated for an appropriate time (**Table I**), under solvent-free conditions to give the products **3a-r** in good to excellent yields (81-93%). The yields of the products are very high under microwave irradiation conditions as compared to the conventional method (**Table I**). The reaction was also performed in the absence of the catalyst under microwave irradiation conditions, but the isolated yields were only 20-30%, indicating that this is indeed a $ZrOCl_2.8H_2O$ catalyzed reaction. The use of smaller amounts of catalyst (2 mole% or 5 mole%) resulted in longer time taken for completion of the reaction. All the products were characterized by IR, NMR, MS and elemental analyses.

The scope and generality of this transformation is illustrated with different *o*-phenylenediamines and orthoesters and the results are summarized in **Table I**. Initially, a mixture of *o*-phenylenediamine (1.0 mmole), triethyl orthoformate (7.2 mmole) and a catalytic amount of $ZrOCl_2.8H_2O$ (10 mole%) was irradiated in a microwave oven for 6 min, and the product **3a** was isolated by column chromatography in 91% yield (entry 1, **Table I**). A wide range of *o*-phenylenediamines was reacted with orthoesters under the described conditions to give the respective benzimidazole derivatives in good to excellent yields (entries 2-18).

Experimental Section

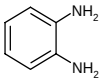
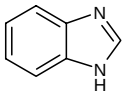
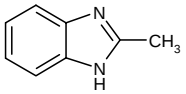
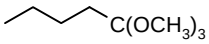
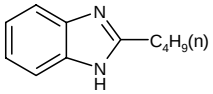
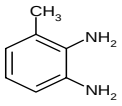
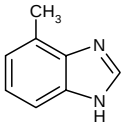
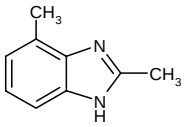
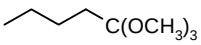
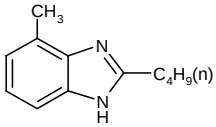
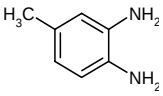
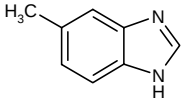
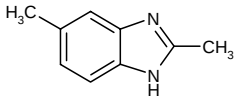
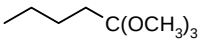
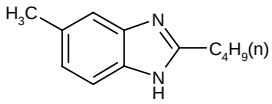
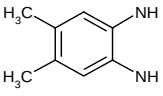
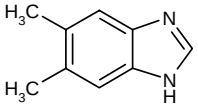
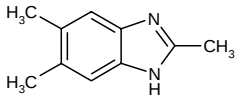
Melting points were determined on a Fisher-Johns melting point instrument and are uncorrected. IR spectra were obtained on a Perkin-Elmer FTIR 5000 spectrometer, using KBr pellets and reported in cm^{-1}. ^1H and ^{13}C NMR spectra were obtained with Varian Gemini (^1H: 300 MHz, ^{13}C: 75 MHz) spectrometer and the chemical shifts are reported in parts per million (δ, ppm) downfield from TMS and coupling constants (*J*) in Hz. Mass spectra were obtained on a VG Micro mass 7070H spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 CHN elemental analyzer. For the microwave irradiation, a conventional household microwave oven (LG Electronics, India) was used.

General procedure for the synthesis of 2- substituted benzimidazoles, 3

A. Conventional method: A mixture of an appropriate *o*-phenylenediamine **1** (1.0 mmole), orthoester **2** (7.2 mmole) in EtOH (5 mL) was stirred at RT in the presence of $ZrOCl_2.8H_2O$ (32 mg, 10 mole%) for an appropriate time (**Table I**). After completion of the reaction, as indicated by TLC, the solvent was removed under reduced pressure and the resulting crude product was chromatographed over silica gel column eluting with 15% EtOAc in pet-ether to afford pure product **3**.

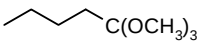
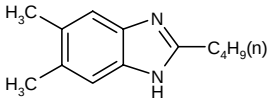
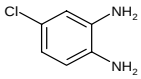
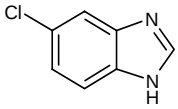
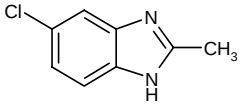
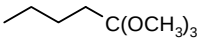
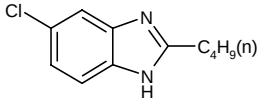
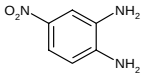
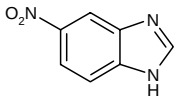
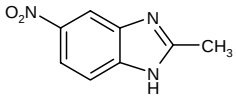
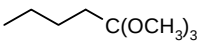
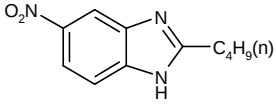
B. Microwave irradiation method: A mixture of an appropriate *o*-phenylenediamine **1** (1.0 mmole), orthoester **2** (7.2 mmole), and $ZrOCl_2.8H_2O$ (32 mg, 10 mole%) were placed in a cylindrical quartz tube. The reaction-mixture was then stirred and irradiated in a microwave oven at 160 W for an appropriate time (**Table I**). After cooling to RT, the resulting crude product was chromatographed over silica gel column eluting with 15% EtOAc in pet-ether to afford pure product **3**.

Table I — Synthesis of 2-substituted benzimidazole by $ZrOCl_2.8H_2O$ catalyzed ring closure reaction

Entry	Diamine	Orthoester	Reaction time		Product		Yield (%)	
			A (hr)	B (min)			A	B
1		$HC(OC_2H_5)_3$	3.0	6		**3a**	77	91
2	〃	$CH_3C(OC_2H_5)_3$	2.0	5		**3b**	73	92
3	〃		3.5	7		**3c**	71	90
4		$HC(OC_2H_5)_3$	3.0	6		**3d**	78	91
5	〃	$CH_3C(OC_2H_5)_3$	2.0	5		**3e**	71	89
6	〃		3.5	7		**3f**	69	86
7		$HC(OC_2H_5)_3$	3.5	7		**3g**	70	89
8	〃	$CH_3C(OC_2H_5)_3$	1.5	5		**3h**	73	93
9	〃		3.0	7		**3i**	72	93
10		$HC(OC_2H_5)_3$	3.0	7		**3j**	80	92
11	〃	$CH_3C(OC_2H_5)_3$	1.5	5		**3k**	80	91

—Contd

Table I — Synthesis of 2-substituted benzimidazole by $ZrOCl_2.8H_2O$ catalyzed ring closure reaction—*Contd*

Entry	Diamine	Orthoester	Reaction time A (hr)	Reaction time B (min)	Product		Yield (%) A	Yield (%) B
12	″		3.0	7		**3l**	72	90
13		$HC(OC_2H_5)_3$	6.0	10		**3m**	69	83
14	″	$CH_3C(OC_2H_5)_3$	3.0	7		**3n**	63	84
15	″		4.5	8		**3o**	64	85
16		$HC(OC_2H_5)_3$	6.0	10		**3p**	72	90
17	″	$CH_3C(OC_2H_5)_3$	4.5	8		**3q**	70	88
18	″		6.0	10		**3r**	62	81

A: RT; B: microwave irradiation.

2-Butyl-1*H*-benzo[*d*]imidazole, 3c: Yellow solid, m.p. 149-50°C; IR (KBr): 3380, 3010, 2944, 1625, 1587, 1410 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, 3H, *J* = 7.1 Hz, CH_3), 1.40 (sext, 2H, *J* = 7.1, 7.4 Hz, CH_2), 1.77 (quin, 2H, *J* = 7.0, 7.4 Hz, CH_2), 2.96 (t, 2H, *J* = 7.1 Hz, CH_2), 7.26-7.52 (m, 4H, Ar-H), 9.33 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 22.9, 24.3, 29.0, 113.1, 121.7, 136.3, 160.1; MS: *m/z* 175 (M^++1). Anal. Calcd. for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 74.90; H, 8.0; N, 15.93%.

2-Butyl-4-methyl-1*H*-benzo[*d*]imidazole, 3f: Pale yellow solid, m.p. 121-23°C; IR (KBr): 3400, 3014, 2982, 1620, 1592, 1410 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, 3H, *J* = 7.1 Hz, CH_3), 1.37 (sext, 2H, *J* = 7.2, 7.4 Hz, CH_2), 1.76 (quin, 2H, *J* = 7.2, 7.4 Hz, CH_2), 2.43 (s, 3H, CH_3), 2.93 (t, 2H, *J* = 7.2 Hz, CH_2), 7.10-7.40 (m, 3H, Ar-H), 8.92 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 20.6, 22.8, 24.7, 29.2, 112.3, 117.2, 132.3, 136.3, 139.3, 161.2; MS: *m/z* 189 (M^++1); Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88. Found: C, 76.03; H, 8.11; N, 14.52%.

2-Butyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole, 3l: Yellow solid, m.p. 116-18°C; IR (KBr): 3412, 3015, 2944, 1625, 1590, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, 3H, *J* = 7.1 Hz, CH_3), 1.36 (sext, 2H, *J* = 7.1, 7.6 Hz, CH_2), 1.75 (quin, 2H, *J* = 7.1, 7.6 Hz, CH_2), 2.37 (s, 6H, CH_3), 2.92 (t, 2H, *J* = 7.1 Hz, CH_2), 7.39 (s, 2H, Ar-H), 9.79 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 19.7, 22.8, 24.7, 29.1, 111.7, 121.9, 134.9, 136.3, 139.3, 160.6; MS: *m/z* 203 (M^++1). Anal. Calcd. for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.01; H, 8.82; N, 13.67%.

2-Butyl-5-chloro-1*H*-benzo[*d*]imidazole, 3o: Yellow solid, m.p. 140-42°C; IR (KBr): 3410, 3018, 2956, 1622, 1583, 746 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$): δ 0.86 (t, 3H, J = 7.1 Hz, CH_3), 1.37 (sext, 2H, J = 7.1, 7.6 Hz, CH_2), 1.79 (quin, 2H, J = 7.1, 7.6 Hz, CH_2), 2.95 (t, 2H, J = 7.1 Hz, CH_2), 7.16 (d, 1H, J = 8.7 Hz, Ar-H), 7.41 (d, 1H, J = 8.7 Hz, Ar-H), 7.50 (s, 1H, Ar-H), 9.90 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 22.8, 24.7, 29.2, 116.2, 117.1, 119.7, 127.3, 137.6, 139.1, 160.3; MS: *m/z* 209 (M^+). Anal. Calcd. for $C_{11}H_{13}ClN_2$: C, 63.31; H, 6.28; N, 13.42. Found: C, 63.09; H, 6.09; N, 13.33%.

The other 2-substituted benzimidazoles reported in **Table I** are known compounds for which satisfactory spectroscopic data were obtained.

Conclusion

In summary, a mild and efficient method has been developed for the synthesis of 2-substituted benzimidazoles from *o*-phenylenediamines and orthoesters in good yields using catalytic amount of $ZrOCl_2.8H_2O$ at RT as well as under solvent-free microwave irradiation conditions. The yields of the products are much higher under microwave irradiation conditions as compared to the yields obtained under conventional method at RT. This approach allows for the preparation of a diverse range of 2-substitued benzimidazoles.

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