AN EFFICIENT AND ECO-FRIENDLY SYNTHESIS OF 2-ARYL-BENZIMIDAZOLES USING SILICA GEL AS CATALYST

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An efficient and eco-friendly method for synthesis of 2-arylbenzimidazoles has been developed simply by grinding intimate mixtures of *ortho*-phenylenediamine, aromatic aldehyde and TLC grade silica gel at room temperature for 30-50 minutes. This one pot synthesis involves aerial oxidation of an intermediate 2-arylbenzimidazoline formed by condensation of the reactants followed by cyclization.

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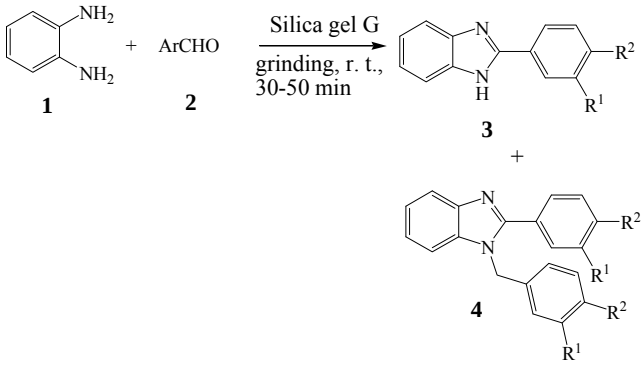
Introduction

Benzimidazoles represent a class of medicinally important nitrogen heterocycles which have wide variety of biological and pharmacological activities such as analgesic,[1] antiamoebic,[2] antimicrobial,[3] antihypertensive,[4] antiparasitic,[5] anti-inflammatory[6] and antitumor[7] activities. *N*-Ribosyl-dimethylbenzimidazole serves as an axial ligand for cobalt in vitamin B_{12}. Benzimidazole derivatives exhibit significant activity against several viruses such as HIV,[8] human cytomegalovirus (HCMV),[9] influenza,[10] etc. A good number of methods have been reported in the literature for the synthesis of 2-substituted benzimidazoles using *o*-phenylenediamines and aldehydes as precursors. Many of the reported methods require long reaction time, use of expensive catalysts and organic solvents.[11-19] The current literature shows that there has been a growing trend towards green synthesis of these compounds.[20-22] The recent trend towards development of solvent-free reaction conditions for organic synthesis[23-27] encouraged us to study the same reaction at room temperature without use of any solvent. Thus, we have been successful in achieving an efficient and eco-friendly synthesis of 2-arylbenzimidazoles simply by grinding an intimate mixture of *ortho*-phenylenediamine and aromatic aldehyde over TLC grade silica gel in open air, which is presented herein.

Results and Discussion

When an intimate mixture of *ortho*-phenylenediamine (**1**) and an aromatic aldehyde (**2**) (1:1 mole ratio) was ground over TLC grade silica gel (silica gel G) in open air, it was found to be converted smoothly to corresponding 2-arylbenzimidazole (**3**) within 30-50 minutes. In some combinations 1-benzyl-2-arylbenzimidazoles (**4**) were also resulted as minor product (Scheme 1, Table 1).



1 **2**

3a Ar=C_6H_5, **3b** Ar=4-BrC_6H_4, **3c** Ar=2-ClC_6H_4, **3d** Ar=4-ClC_6H_4, **3e** Ar=4-MeC_6H_4, **3f** Ar=4-MeOC_6H_4, **3g** Ar=3,4-OCH_2O-C_6H_3, **3h** Ar=2-$NO_2C_6H_4$, **3i** Ar=4-$NO_2C_6H_4$, **3j** Ar=4-$Me_2NC_6H_4$, **3k** Ar=2-pyridyl, **3l** Ar=2-thienyl, **4a** Ar=C_6H_5; **4e** Ar=4-MeC_6H_4, **4f** Ar=4-MeOC_6H_4

Scheme 1. Synthesis of benzimidazoles from of *o*-phenylene-diamine and aromatic aldehydes.

The scope of recyclability of the silica gel G catalyst was then investigated. It has been observed that the catalyst can be recovered after completion of the reaction and it can be used further with no significant loss of activity (Table 2).

The mechanisms for formation of 2-arylbenzimida-zoles (**3**) and 1-arylmethyl-2-arylbenzimidazoles (**4**) from **1** and **2** have been discussed in a number of recent papers[14,16,28]. From the mechanisms suggested therein (Scheme 2), it is observed that the formation of **3** requires an oxidation (aerial or catalytic) of an intermediate 2-arylbenzimidazoline (**6**). For the formation of **4**, 2 molar proportion of aldehyde is required and here the conversion of the intermediate diimine **7** to the product takes place by cyclization followed by intramolecular hydride transfer. In the method being reported, it is observed that in cases of use of aromatic aldehydes containing electron withdrawing groups, 2-arylbenzimidazoles (**3**) are formed as the only product even if 2 molar proportion of the aldehyde is used. This result suggests that for reactions involving such aldehydes cyclization of 2-benzalaminoanilines (**5**) (Step 1a) is significantly faster than their reaction with another molecule of aldehyde (Step 2).

Table 1. Synthesis of benzimidazoles under solvent-free conditions

Entry	Ar in ArCHO	Time, min	Mole ratio of the reactants 2 and 1			
			1:2		1:1	
			Yield of 3, %[a]	Yield of 4, %[a]	Yield of 3, %[a]	Yield of 4, %[a]
1.	C_6H_5	40	49	17	45	15
2.	4-BrC_6H_4	30	89	0	91	0
3.	2-ClC_6H_4	30	94	0	96	0
4.	4-ClC_6H_4	30	89	0	92	0
5.	4-MeC_6H_4	45	47	14	43	10
6.	4 -$MeOC_6H_4$	45	46	17	45	10
7.	3,4(OCH_2O)C_6H_3	45	67	5	62	6
8.	2- $O_2NC_6H_4$	30	86	0	84	0
9.	4- $O_2NC_6H_4$	45	74	0	71	0
10.	4-$Me_2NC_6H_4$	45	63	0	60	0
11.	2-pyridyl	30	76	0	74	0
12.	2-thienyl	30	79	0	78	0

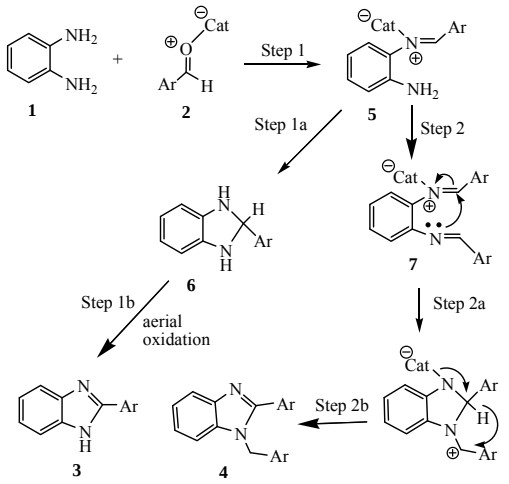
[a] Isolated yield with respect to the amount of **1.**

Table 2. Recyclability of the catalyst[a]

No. of cycles	Reaction time, min	Yield,%[b] of 3c (using 1 and 2-ClC_6H_4CHO)	Yield, %[b] of 3d (using 1 and 4-ClC_6H_4CHO)
Fresh	30	96	92
Run 1	30	94	89
Run 2	35	92	88
Run 3	35	91	86

[a] In each time the reaction was carried out by grinding an intimate mixture of **1 (**1 mmol), **2** (aldehyde, 1 mmol) and silica gel G (4 g) in open air at room temperature. [b]Isolated yield with respect to the amount of **1.**

For use of aromatic aldehydes without having any electron withdrawing group, the said cyclization is relatively slower and that ultimately widens the possibility of formation of **4** as a minor product.



Scheme 2. Suggested mechanisms for formation of benzimidazoles from of *o*-phenylenediamine and aromatic aldehydes.

In the present method it is a common observation that the reactions are very clean, and the crude products obtained in the entries 2-4 and 8-12 were pure enough. Their crystallization from ethyl acetate-petroleum ether was sufficient to provide analytically pure samples of **3**.

The crude product obtained in each of the other entries could be resolved into two pure products (**3** and **4**) by a single column chromatography over silica gel.

Experimental

General.

Melting points were recorded on a Köfler block. IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer (Spectrum BX II) in KBr pellets. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and in DMSO-d_6 on a Bruker AV-300 (300 MHz) spectrometer. Analytical samples were routinely dried *in vacuo* at room temperature. Microanalytical data were recorded on two Perkin-Elmer 2400 Series II C, H, N analyzers. HRMS were measured with a Waters HRMS instrument [Xevo G2QTof] spectrometer. Column chromatography was performed with silica gel (100-200 mesh) and TLC with silica gel G made of SRL Pvt. Ltd. Petroleum ether had the boiling range 60-80 °C.

General method for synthesis of benzimidazole derivatives (3 and 4).

An intimate mixture of *o*-phenylenediamine (**1,** 1 mmol), an aromatic aldehyde (**2,** 1 mmol) and silica gel G (4g, quality mentioned above) was taken in a mortar and it was ground in open air at room temperature for the time period mentioned in Table 1. The progress of the reaction was monitored by TLC over silica gel. When the reaction was found to be complete, the reaction mixture was washed thoroughly with ethyl acetate. The crude material obtained by concentration of this ethyl acetate extract on crystallization from ethyl acetate-petroleum ether gave pure 2-arylbenzimidazoles (**3**) in the entries 2-4 and 8-12 (Table 1). The similar material obtained in each of the other entries was subjected to column chromatography over silica gel which resulted in separation of the products **3** and **4**. These two products were finally crystallized from ethyl acetate-petroleum ether.

All the products **3a-l** were known compounds and they were characterised by comparison of their physical and spectral data with those reported in literature.

Compound 3a.

Colourless needles, m.p. 287-288 °C (lit.[14] 288-289 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.22 (br. s, 2H), 7.50-7.56 (m, 4H), 7.67 (1H, br. d, J = 7.1 Hz), 8.18 (d, 2H, J = 7.2 Hz), 12.93 (br. s, 1H).

Compound 3b.

Colourless needles, m.p. 297-298 °C (lit.[30] 299-300 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.24 (br. s, 2H), 7.52-7.72 (m, 2H), 7.76 (d, 2H, J = 8.4Hz), 8.12 (d, 2H, J = 8.4 Hz), 13.02 (br. s, 1H).

Compound 3c.

Colourless needles, m.p. 225-227 °C (lit.[14] 227-229 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.18-7.26 (m, 2H), 7.47-7.56 (m, 3H), 7.62 -7.69 (m, 2H), 7.87-7.90 (m, 1H), 12.70 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 111.8, 119.4, 123.3, 128.6, 129.4, 129.5, 135.0, 135.5, 144.2, 150.6.

Compound 3d.

Colourless needles, m.p. 281-282 °C (lit.[14] 281-283 °C).; IR (KBr): ν_{max} = 3338, 2923, 1624, 1448, 1487 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.17-7.26 (m, 2H), 7.54 (br. d, 1H, J = 7.5 Hz), 7.62-7.69 (m, 3H), 8.18 (d, 2H J = 8.7 Hz), 12.99 (br. s, 1H).

Compound 3e.

Colourless needles, m.p. 292-293 °C (lit.[14] 293-294 °C).; IR (KBr): ν_{max} = 3340, 3016, 2854, 1625, 1439, 1288 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.39 (s, 3H), 7.20 (br. s, 2H), 7.37 (d, 2H, J = 7.5 Hz), 7.59 (br. s, 2H), 8.07 (d, 2H, J = 7.8 Hz), 12.83 (br. s, 1H). HRMS $(M+H)^+$ Calcd. for $C_{14}H_{12}N_2$: 209.26; Found: 209.13. Anal. Calcd. for $C_{14}H_{12}N_2$ (208.26): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.56; H, 5.61; N, 13.21%.

Compound 3f.

Colourless needles, m.p. 230-231°C (lit.[14] 231°C). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.82 (s, 3H), 7.10 (d, 2H, J = 8.7 Hz), 7.14-7.16 (m, 2H), 7.47 (d, 2H, J = 6.2 Hz), 7.59 (d, 1H, J = 6.6 Hz), 8.09 (d, 2H, J =8.7 Hz), 12.72 (br. s, 1H),

Compound 3g.

Colourless needles, m.p. 251-252°C (lit.[29] 252 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.10 (s, 2H), 7.07 (d, 1H, J = 8.1 Hz), 7.17 (br. s, 2H), 7.48 (br. d, 1H, J = 6.5 Hz), 7.60 (br. d, J = 6.6 Hz, 1H), 7.66-7.71 (m, 2H), 12.73 (br. s, 1H).

Compound 3h.

Colourless needles, m.p. 211°C (lit.[29] 210 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.24 (br. s, 2H), 7.62 (br. s, 2H), 7.74 (t, 1H, J = 7.5 Hz), 7.85 (t, 1H, J = 7.5 Hz), 7.96 (d, 1H, J = 7.5 Hz), 8.01 (d, 1H, J = 7.8 Hz), 13.04 (br. s, 1H),

Compound 3i.

Colourless needles, m.p. 316 °C (lit.[29] 316 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.26 (br. s, 2H), 7.59 (br. s, 1H), 7.71 (br. s, 1H), 8.39 (s, 4H), 13.30 (br. s, 1H).

Compound 3j.

Colourless needles, m.p. 291-292 °C (lit.[14] 292-294 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.04 (s, 6H), 6.77 (d, 2H, J = 8.7 Hz), 7.20-7.23 (m, 2H), 7.60 (br. s, 2H), 7.92 (d, 2H, J = 8.7 Hz).

Compound 3k.

Colourless needles, m.p. 218-219°C (lit.[29] 218 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28-7.31 (m, 2H), 7.37 (t, 1H, J = 6.6 Hz), 7.48 (br. s, 1H), 7.84-7.90 (m, 2H), 8.45 (d, 1H, J = 7.8 Hz), 8.63 (d, 1H, J = 4.5 Hz), 10.88 (br. s, 1H).

Compound 3l.

Colourless needles, m.p. 331-332 °C (lit.[30] 332 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.16 (t, 1H, J = 4.2 Hz), 7.24-7.29 (m, 3H), 7.47 (d, 1H, J = 5.1 Hz), 7.62 (d, 2H, J = 3.3 Hz).

Compound 4a.

Colourless needles, m.p. 135-136°C (lit.[28] 135-136 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.46 (s, 2H), 7.11 (br. d, 2H, J = 7.8 Hz), 7.19-7.26 (m, 2H), 7.28-7.36 (m, 4H), 7.45-7.50 (m, 3H), 7.69 (dd, 2H, J = 7.5 Hz and 2.4 Hz), 7.87 (d, 1H, J = 8.1Hz).

Compound 4e.

Colourless needles, m.p. 131-132 °C (lit.[28] 132-133 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 2.43 (s, 3H), 5.43 (s, 2H), 7.02 (d, 2H, J = 7.8 Hz), 7.16 (d, 2H, J = 7.8 Hz), 7.21-7.35 (m, 5H), 7.61 (d, 2H, J = 8.0 Hz), 7.88 (d, 1H, J = 7.8 Hz). HRMS $(M+H)^+$ Calcd for $C_{22}H_{20}N_2$: 313.16; Found: 313.19. Anal. Calcd. for $C_{22}H_{20}N_2$ (312.16): C, 84.58; H, 6.45; N, 8.97. Found: C, 84.31; H, 6.33; N, 8.78%.

Compound 4f.

Colourless needles, m.p. 130-131°C (lit.[28] 131-132 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.78 (s, 3H), 3.85 (s, 3H), 5.38 (s, 2H), 6.84 (d, 2H, J = 8.7 Hz), 6.97 (d, 2H, J = 8.7 Hz), 7.03 (d, 2H, J = 8.5 Hz), 7.21-7.32 (m, 3H), 7.64 (d, 2H, J = 8.7 Hz), 7.84 (d, 1H, J = 8.7 Hz).

Recovery of the catalyst.

The catalyst separated from the reaction mixture was washed thoroughly with ethyl acetate till the washings became almost colourless. It was then dried in a hot air oven at 100 °C for 1h. The dried catalyst was cooled to room temperature and then used further.

Conclusion

We report here a very simple, efficient and eco-friendly method for synthesis of 2-arylbenzimidazoles (**3**) avoiding the use of any solvent. The sets yielding **3** as the only product did not require any chromatographic purification.

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