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REGULAR ARTICLE

Sodium dichloroiodate promoted C-C bond cleavage: An efficient synthesis of 1,3-Benzazoles via condensation of *o*-amino/mercaptan/hydroxyanilines with *β*-diketones

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Abstract. An efficient aqueous sodium dichloroiodate ($NaICl_2$) mediated protocol is developed for the synthesis of benzofused azoles by the cyclization of 2-amino anilines/thiophenols/phenols with *β*-diketone compounds. The reactions gave moderate to good yield of the corresponding 2-substituted benzimidazoles/benzothiazoles/benzoxazoles under mild conditions. This tandem process involved a C-C bond cleavage and C-N bond formation.

Keywords. Benzimidazole/benzothiazole/benzoxazole; *β*-diketones; $NaICl_2$; C-C bond cleavage.

1. Introduction

Nitrogen-containing five-member heterocyclic rings, such as benzoxazoles, benzthiazoles and benzimidazoles, are widely distributed in nature and are important fragments in medicinal chemistry because of their wide range of biological activities, for example anticancer, anti-inflammatory, antimicrobial, and antiviral.[1–6] They are also found in number of commercially available drugs (albendazole, omeprazole, pimobendan, mebendazoleand phortress).[7] Moreover, benzofused azoles are also widely used in dyes, agrochemicals, chemosensing, and fluorescence.[8–10] Therefore, the development of efficient methods for the synthesis of benzofused azoles has been receiving considerable attention in recent years.

A range of methods are available for synthesis of these heterocycles, including condensation of *o*-phenylenediamine, *o*-aminophenol, or *o*-aminobenzenethiol, with aldehydes/carboxylic acids or their equivalents including acid chlorides, amides, nitriles, orthoesters, and *β*-ketoesters.[11–25] All these methods involve the use of strong oxidative conditions, high temperature, strong proton acids, and/or microwave irradiation for high yields. Another method involves the transition-metal-catalyzed intramolecular cyclization of 2-haloanilides analogues.[26–30] Despite many methodologies for the synthesis of benzofused azoles, some of them suffer from one or more shortcomings, such as complicated catalyst, long reaction time, expensive and/or non-commercially available starting materials, transition metal catalyst, use of oxidant, and/or harsh conditions. Therefore, the development of novel and more effective synthetic strategies is undoubtedly attractive and desirable. Recently, *p*-toluene sulfonic acid ($TsOH \cdot H_2O$) has been utilized for the synthesis of benzothiazoles/benzimidazoles from *β*-diketones and 2-aminothiophenols/2-aminoanilines respectively,[31] however, this method is not useful for the synthesis of benzoxazoles, the same authors later reported the synthesis of benzoxazoles from 2-aminophenol and *β*-diketones using a combination of *p*-toluene sulfonic acid ($TsOH{\cdot}H_2O$) and copper iodide (CuI).[32] This result motivated us to explore a single metal free protocol for the synthesis of these 1,3-benzazoles, benzimidazoles/benzothiazoles/benzoxazoles, using *β*-diketones and *o*-amino anilines/thiophenols/phenols.

Carbon–carbon bonds are ubiquitous in organic compounds. Compared to the highly developed C-C bond forming reactions, the cleavage of C-C single bonds is the most challenging issue in organic chemistry due to their inert nature, thermodynamic stability and

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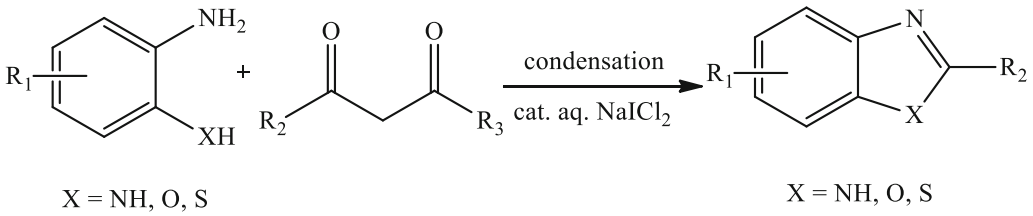


Scheme 1. Single protocol for the synthesis of 2-substituted 1,3-benzazoles from β-diketones.

uncontrollable selectivity. Thus the cleavage of C-C bond has emerged as a challenging and attractive area which provides new modes of chemical reactivity to synthetic organic chemistry. To cleave unstrained inert C-C bonds, harsh conditions with stoichiometric oxidants, such as peroxides and toxic metal salts including transition metals are frequently employed.[33–36] Sodium dichloroiodate is a commercially available iodine reagent previously investigated in our laboratory for a number of varied organic transformations.[37–39] This prompted us to explore the feasibility of this versatile reagent for C-C bond cleavage. Herein, in continuation of our ongoing research on the synthesis of *N*-heterocycles, we report an efficient method for the synthesis of benzofused azoles *via* $NaICl_2$ catalyzed C-C bond cleavage of β-diketones (Scheme 1).

2. Experimental

2.1 *Materials and methods*

All the chemicals and reagents were purchased from Sigma Aldrich, SD fine, Avra Synthesis or Spectrochem companies and were used without further purification. Solvents were distilled from an appropriate drying agent. The purity determination of the starting materials and reaction monitoring was accomplished by thin-layer chromatography (TLC) on Merck silica gel 60 F_{254} plates. Silica gel 60–120 mess was used for column chromatography. Melting points of all the compounds were recorded on Thermomik Campbell melting point apparatus having an oil bath system and are uncorrected. The FT-IR spectra (KBr) were recorded on Shimadzu FTIR Affinity-1 Fourier Transform Infrared spectrophotometer. ^{1}H NMR spectra were recorded on MR400 Agilent Technology NMR spectrometer (400 MHz) using tetramethylsilane (TMS) as internal standard and DMSO-d_6/$CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvent peaks and coupling constants (J) are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t). Splitting patterns that could not be interpreted is designated as multiplet (m). All the products are known compounds and were identified by ^{1}H NMR spectroscopy.

2.2 *General procedure for the synthesis of 2-substituted 1,3-Benzazoles* **3**, **5** *and* **7**

To a mixture of *o*-substituted (–NH_2 or –SH or –OH) anilines (1.0 mmol) and appropriate 1,3-diketones (1.1 mmol) in THF (5 mL) was added 30%$^w/_w$ aqueous $NaICl_2$ (0.2 mmol, 20 mol%). The reaction was allowed to remain stirred at reflux temperature for 2–3 h. After the reaction was complete, as indicated by TLC, the mixture was cooled to room temperature. The volatiles were removed under reduced pressure and treated successively with aqueous sodium thiosulphate solution and saturated solution of $NaHCO_3$, and extracted by ethylacetate (2×10 mL). The combined organic phases were washed with brine and dried over Na_2SO_4 and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluents.

2.2a *2-Methyl-1H-benzimidazole* **3a**[40]: Yield 90%, White solid, M.p. 173–175 °C (Lit. 174–176 °C); FT-IR (KBr): υ 3420, 3110, 2985, 1630, 1560, 1450, 1370, 1275, 1215, 1047, 846, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.21 (brs, 1H, NH), 7.52–7.48 (m, 2H, ArH), 7.22–7.19 (m, 2H, ArH), 2.59 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 138.6, 122.1, 114.6, 14.9. HRMS: calcd for $C_8H_8N_2$: 132.0687, found 132.0687.

2.2b *2-Ethyl-1H-benzimidazole* **3b**[31]: Yield 95%, White solid, M.p. 171–173 °C (Lit. 171–173 °C); FT-IR (KBr): υ 3417, 2996, 1614, 1540, 1430, 1365, 1274, 1224, 1045, 887, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.3 (brs, 1H, NH), 7.58–7.55 (m, 2H, ArH), 7.26–7.20 (m, 2H, ArH), 2.99 (q, J = 7.6 Hz, 2H, CH_2), 1.47 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 138.7, 122.1, 114.6, 22.9, 12.4. HRMS: calcd for $C_9H_{10}N_2$: 146.0844, found 146.0845.

2.2c *2-Isopropyl-1H-benzoimidazole* **3c**[31]: Yield 55%, White solid, M.p. 235–237 °C (Lit. 234–236 °C); FT-IR (KBr): υ 3410, 2996, 1620, 1510, 1415, 1365, 1286, 1224, 1088 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (brs, 1H, NH), 7.58-7.56 (m, 2H, ArH), 7.23–7.16 (m, 2H, ArH), 3.30–3.22 (m, 1H, CH), 1.49 (t, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 138.9, 122.1, 115.4, 30.3, 22.1. HRMS: calcd for $C_{10}H_{12}N_2$: 160.1000, found 160.1000.

Table 1. Screening of Reaction Conditions[a].

Entry	$NaICl_2$ (mol%)	Temperature	Time (h)	Yield(%)[b]
1	None	rt	24	NR[c]
2	100	rt	5	60
3	100	Reflux	2	88
4	50	Reflux	2	93
5	**20**	**Reflux**	**2**	**90**
6	10	Reflux	5	58

[a]Reaction conditions: *o*-phenylenediamine (**1a**, 1.0 mmol), 2,4-pentanedione (**2a**, 1.1 mmol), 30% aqueous $NaICl_2$ catalyst in tetrahydrofuran (5.0 mL). [b]Isolated yield. [c]No reaction

2.2d *2,5-Dimethyl-1H-benzimidazole* **3d**[41]: Yield 84%, White solid, M.p. 200–202 °C (Lit. 202–203 °C); FT-IR (KBr): υ 3420, 3040, 2915, 2765, 1620, 1550, 1480, 1281, 1034, 877, 791 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.04 (brs, 1H, NH), 7.43 (d, J = 7.9 Hz, 1H, ArH), 7.33 (s, 1H, ArH), 7.02 (d, J = 7.9 Hz, 1H, ArH), 2.62 (s, 3H, CH_3), 2.41 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 138.3, 136.7, 132.6, 124.4, 114.5, 114.3, 22.1, 14.9. HRMS: calcd for $C_9H_{10}N_2$: 146.0844, found 146.0847.

2.2e *2-Ethyl-5-methyl-1H-benzimidazole* **3e**[31]: Yield 93%, White solid, M.p. 160–163 °C (Lit. 160–162 °C); FT-IR (KBr): υ 3421, 3010, 2985, 2740, 1630, 1554, 1421, 1320, 1277, 1138, 1070, 970, 873, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.26 (brs, 1H, NH), 7.45 (d, J = 8.4 Hz, 1H, ArH), 7.34 (s, 1H, ArH), 7.06 (d, J = 8.4 Hz, 1H, ArH), 2.99 (q, J = 7.6 Hz, 2H, CH_2), 2.43 (s, 3H, CH_3), 1.42 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 137.4, 135.9, 130.8, 113.3, 113.0, 122.5, 21.6, 20.4, 11.4. HRMS: calcd for $C_{10}H_{12}N_2$: 160.1000, found 160.1001.

2.2f *5-Chloro-2-methyl-1H-benzimidazole* **3f**[42]: Yield 91%, Off white solid, M.p. 202–203 °C (Lit. 200–201 °C); FT-IR (KBr): υ 3414, 3122, 2971, 1634, 1552, 1401, 1279, 1057, 923, 797 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.29 (brs, 1H, NH), 7.51 (s, 1H, ArH), 7.45 (d, J = 8.4 Hz, 1H, ArH), 7.12 (d, J = 8.3 Hz, 1H, ArH), 2.51 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 140.1, 137.1, 126.1, 121.8, 115.4, 114.3, 15.1. HRMS: calcd for $C_8H_7ClN_2$: 166.0298, found 166.0300.

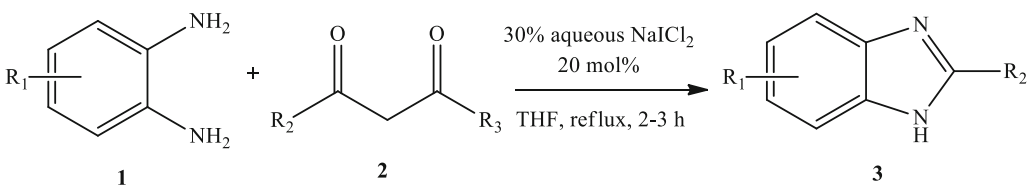
2.2g *5-Chloro-2-ethyl-1H-benzimidazole* **3g**[31]: Yield 95%, Brown solid, M.p. 170–171 °C (Lit. 169–171 °C); FT-IR (KBr): υ 3420, 3130, 3003, 1670, 1572, 1391, 1265, 1100, 921, 804 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.47 (brs, 1H, NH), 7.62 (s, 1H, ArH), 7.51 (d, J = 8.2 Hz, 1H, ArH), 7.18 (d, J = 8.2 Hz, 1H, ArH), 2.91 (q, J = 7.6 Hz, 2H, CH_2), 1.37 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 126.1, 121.8, 119.6, 117.7, 112.4, 111.2, 22.3, 12.7. HRMS: calcd for $C_9H_9ClN_2$: 180.0454, found 180.0454.

2.2h *2-Phenyl-1H-benzimidazole* **3h**[43]: Yield 20%, Yellow solid, M.p. 290–293 °C (Lit. 292–294 °C); FT-IR (KBr): υ 3450, 3045, 1620, 1580, 1458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.80 (s, 1H, NH), 7.56–7.50 (m, 4H, ArH), 7.21–7.15 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 144.5, 135.2, 130.6, 130.3, 129.5, 126.9, 123.1, 122.2, 119.5, 111.7. HRMS: calcd for $C_{13}H_{10}N_2$: 194.0844, found 194.0846.

2.2i *2-Methylbenzothiazole* **5a**[44]: Yield 90%, Pale yellow liquid; FT-IR (KBr): υ 1554, 1521, 1450, 1310, 1232 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)δ 7.97 (d, J = 7.9 Hz, 1H, ArH), 7.81 (d, J = 7.9 Hz, 1H, ArH), 7.44 – 7.41 (m, 1H, ArH), 7.32 – 7.28 (m, 1H, ArH), 2.80 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 151.2, 133.4, 124.0, 122.7, 119.3, 18.1. HRMS: calcd for C_8H_7NS: 149.0299, found 149.0301.

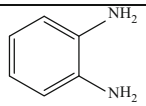
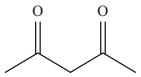
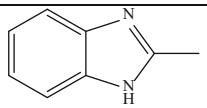
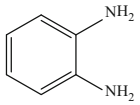
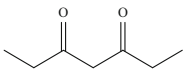
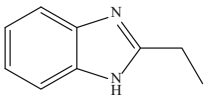
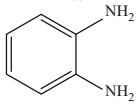
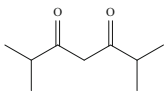
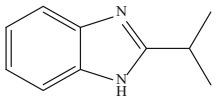
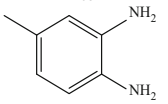
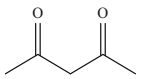
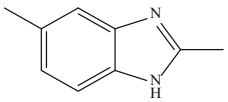
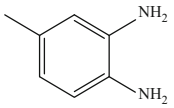
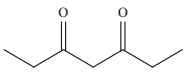
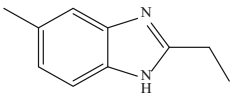
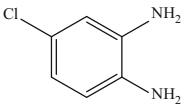
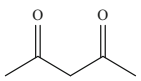
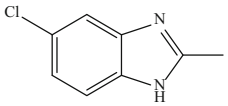
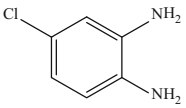
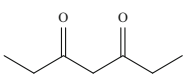
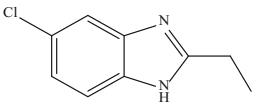
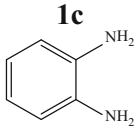
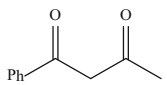
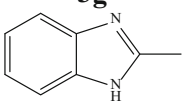
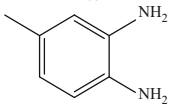
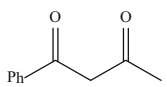
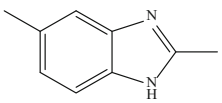
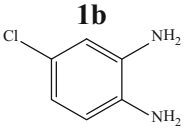
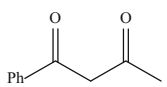
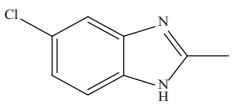
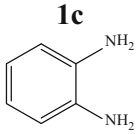
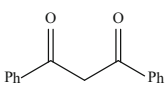
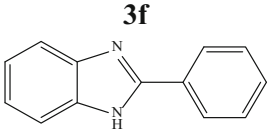
2.2j *2-Ethylbenzothiazole* **5b**[40]: Yield 85%, Yellow liquid; FT-IR (KBr): υ 1565, 1534, 1455, 1320, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 1H, ArH), 7.78 (d, J = 8.0, 1H, ArH), 7.39 (m, 1H, ArH), 7.29 (m, 1H, ArH), 3.11 (q, J = 7.1 Hz, 2H, CH_2), 1.43 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 153.0, 135.2, 125.9, 124.7, 122.6, 121.4, 28.1, 13.8. HRMS: calcd for C_9H_9NS: 163.0456, found 163.0455.

2.2k *5-Chloro-2-methylbenzothiazole* **5c**[31]: Yield 70%, White solid, M.p. 67–69 °C (Lit. 68–69 °C); FT-IR (KBr): υ 1550, 1521, 1440, 1307, 1275, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (m, 1H, ArH), 7.77 (s, 1H, ArH), 7.39 – 7.36 (m, 1H, ArH), 2.79 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 154.7, 134.1, 132.3, 125.5, 122.6, 122.1, 20.3. HRMS: calcd for C_8H_6ClNS: 182.9909, found 182.9907.

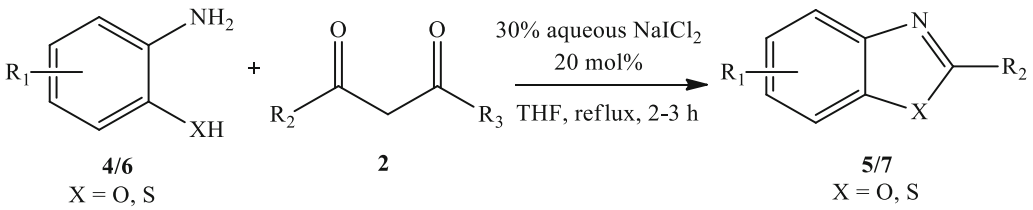


Scheme 2. Reaction between *o*-phenylenediamines and β–diketones in presence of aq. $NaICl_2$.

Table 2. Synthesis of 2-substituted benzimidazole[a].

Entry No.	Substituted 1,2-diamines 1	1,3-diketones 2	Product 3	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	90
2	 **1a**	 **2b**	 **3b**	95
3	 **1a**	 **2c**	 **3c**	55
4	 **1b**	 **2a**	 **3d**	84
5	 **1b**	 **2b**	 **3e**	93
6	 **1c**	 **2a**	 **3f**	91
7	 **1c**	 **2b**	 **3g**	95
8	 **1a**	 **2d**	 **3a**	70
9	 **1b**	 **2d**	 **3d**	74
10	 **1c**	 **2d**	 **3f**	70
11	 **1a**	 **2e**	 **3h**	20/60[c]

[a]Reaction conditions: 1.0 mmol of *o*-phenylenediamine, 1.1 mmol of *β*–diketone and 20 mol% aqueous $NaICl_2$ in tetrahydronfuran at reflux. [b]Isolated yields after column chromatography and structures were confirmed by comparison of IR, ^1H NMR and M.P. with literature reports. [c]Reaction carried in a sealed tube for 10 h.



4/6
X = O, S

2

5/7
X = O, S

Scheme 3. Reaction between *o*-amino phenols/thiophenols and β–diketones in presence of aq. $NaICl_2$.

2.2l *5-Chloro-2-ethylbenzothiazole* **5d**[31]: Yield 65%, Yellow liquid; FT-IR (KBr): υ 1560, 1527, 1445, 1310, 1280, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H, ArH), 7.72 (d, J = 8.1 Hz, 1H, ArH), 7.30 (d, J = 8.1 Hz, 1H, ArH), 3.13 (q, J = 7.5 Hz, 2H, CH_2), 1.46 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 154.4, 133.7, 132.3, 125.4, 122.8, 122.6, 28.4, 13.7. HRMS: calcd for C_9H_8ClNS: 197.0066, found 197.0067.

2.2m *2-Methylbenzoxazole* **7a**[45]: Yield 80%, Yellow liquid; FT-IR (KBr): υ 3050, 2995, 2930, 2851, 1435, 1270, 710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 1H, ArH), 7.42–7.40 (m, 1H, ArH), 7.24-7.21 (m, 2H, ArH), 2.59 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 150.8, 141.4, 124.5, 124.0, 119.3, 110.2, 14.5. HRMS: calcd for C_8H_7NO: 133.0528, found 133.0525.

2.2n *2,5-Dimethylbenzoxazole* **7b**[32]: Yield 67%, Colourless liquid; FT-IR (KBr): υ 3030, 2975, 2856, 1484, 1256, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H, ArH), 7.32 (d, J = 8.1 Hz, 1H, ArH), 7.04 (d, J = 8.1 Hz, 1H, ArH), 2.57 (s, 3H, CH_3), 2.38 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 147.3, 140.2, 130.1, 122.5, 117.6, 107.1, 19.4, 13.3. HRMS: calcd for C_9H_9NO: 147.0684, found 147.0683.

2.2o *2-Methyl-5-chlorobenzoxazole* **7c**[46]: Yield 71%, White solid, M.p. 55–57 °C (Lit. 53–55 °C); FT-IR (KBr): υ 3110, 3093, 2994, 1495, 1260, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H, ArH), 7.34 (d, J = 8.3 Hz, 1H, ArH), 7.23 (d, J = 8.3 Hz, 1H, ArH), 2.61 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 149.4, 142.6, 129.3, 124.7, 119.3, 111.2, 14.8. HRMS: calcd for C_8H_6ClNO: 167.0138, found 167.0141.

3. Results and Discussion

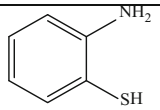
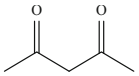
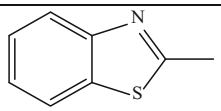
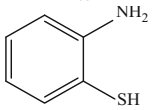
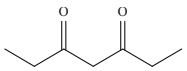
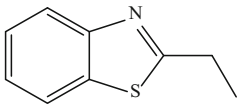
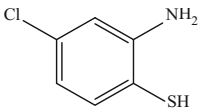
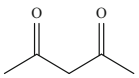
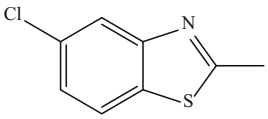
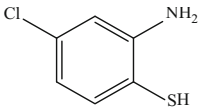
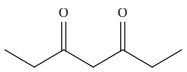
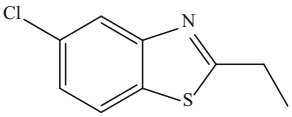
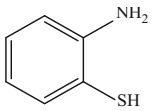
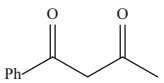
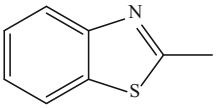
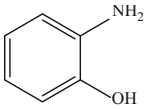
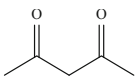
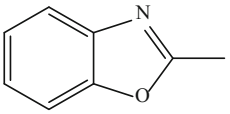
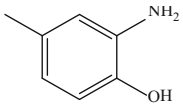
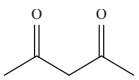
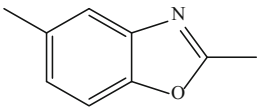
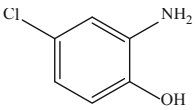
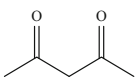
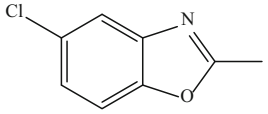
To optimize the reaction conditions, including catalyst loading, temperature, and solvent, the condensation of *o*-phenylenediamine **1a** and 2,4-pentanedione **2a** was used as the model reaction and results are summarized in Table 1.

The desired product, 2-methyl-1*H*-benzimidazole **3a** was obtained when reaction of **1a** with **2a** was performed in tetrahydrofuran (THF) using 1 equivalents of $NaICl_2$ at room temperature in good yield (60%) after 5 hrs stirring (Table 1, entry 2). It was observed that raising the reaction temperature from room temperature to reflux brought about a considerable increase in yield of **3a** (88%) simultaneously reducing the reaction time (Table 1, entry 3). Further, decreasing the quantity of the $NaICl_2$ to 50 mol% or 20 mol% did not affect the product yield and reaction time considerably (Table 1, entry 4–5). A further decrease in the $NaICl_2$ quantity to 10 mol%, however, resulted in relatively low yield (Table 1, entry 6). After testing other solvents, such as acetonitrile, 1,4-dioxane, dichloromethane, methanol, and ethanol, it was found that THF is most suitable solvent for this reaction (Scheme 2).

With the optimum reaction conditions in hand, an exploration of substrate scope was performed with structural varied β-diketones **2** and *o*-phenylenediamines **1** and the results are summarized in Table 2. The reactions proceeded smoothly affording the expected 2-substituted-1*H*-benzimidazoles **3** in moderate to good yields, regardless of the steric hindrance and electronic effect of the substituents. The reactions of *o*-phenylenediamine **1a** with β-diketones **2a**, **2b**, and **2c** bearing aliphatic groups on their 1,3-positions, under optimised reaction conditions, proceeded smoothly to afford the desired 2-substituted-1*H*-benzimidazoles **3** in good yields (Table 2, entry 1-3). The lower yield of the product **3c,** obtained by reacting **1a** with **2c**, may be due to steric hindrance of the bulky *iso*-propyl group of the diketone.

The presence of electron donating group and electron withdrawing group on 2-aminoaniline had an insignificant effect on the reaction yields (Table 2, entry 4–7). Next, the reaction of *o*-phenylenediamine **1a** with unsymmetrical β-diketone, 1-methyl-3-phenyl-1,3-dione **2d**, gave the corresponding 2-methyl-1*H*-benzimidazole **3a** as the major product (Table 2, entry 8), thus indicating the higher reactivity of acetyl group as compared to benzoyl group under the present reaction conditions. The same was ascertained by the reaction of

Table 3. Synthesis of 2-substituted benzothiazole and benzoxazole[a].

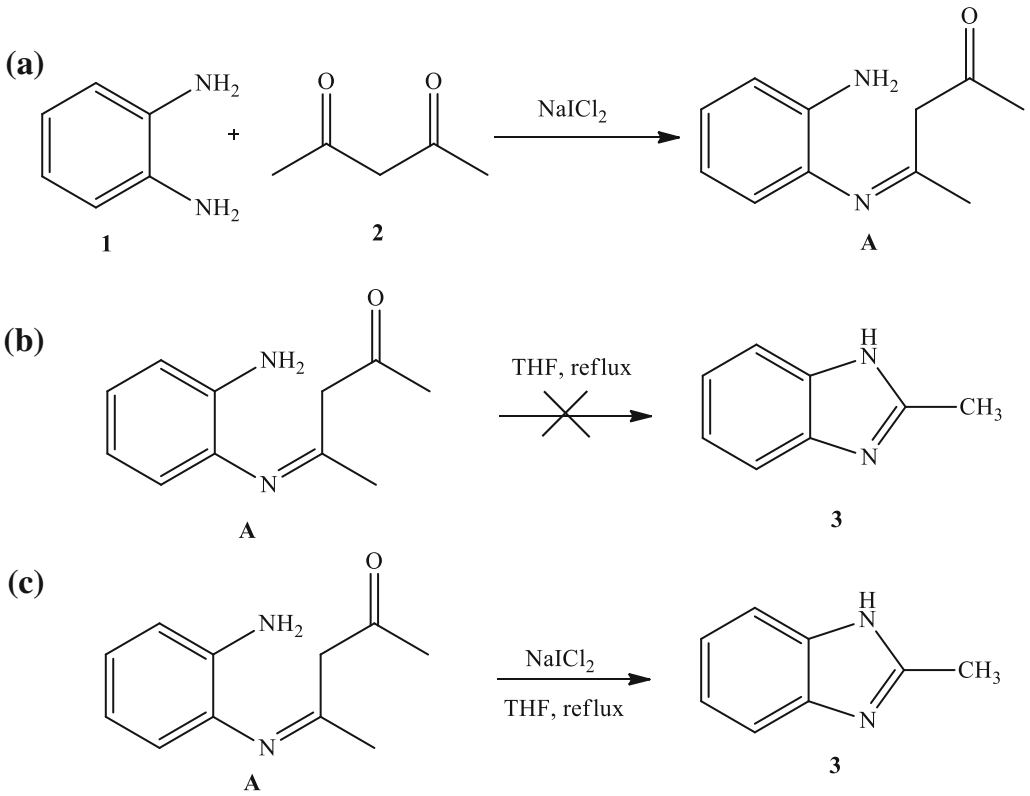
Entry No.	Substituted *o*-amino derivative 4/6	X	1,3-diketones 2	Product	Yield (%)[b]
1	 **4a**	S	 **2a**	 **5a**	90
2	 **4a**	S	 **2b**	 **5b**	85
3	 **4b**	S	 **2a**	 **5c**	70
4	 **4b**	S	 **2b**	 **5d**	65
5	 **4a**	S	 **2d**	 **5a**	57
6	 **6a**	O	 **2a**	 **7a**	80
7	 **6b**	O	 **2a**	 **7b**	67
8	 **6c**	O	 **2a**	 **7c**	71

[a]Reaction conditions: 1.0 mmol of *o*-amino thiophenol/phenol, 1.1 mmol of β–diketone and 20 mol% aqueous $NaICl_2$ in tetrahydronfuran at reflux. [b]Isolated yields after column chromatography and structures were confirmed by comparison of IR, ^{1}H NMR and M.p. with literature reports.

substituted *o*-phenylenediamines with unsymmetrical β-diketone (Table 2, entry 9–10). Further, the low yield of the desired product, 2-phenyl-1*H*-benzimidazole, obtained by treating *o*-phenylenediamine with 1,3-diphenylpropane-1,3-dione, emphasize our claim of low reactivity of the benzoyl group over acetyl group (Table 2, entry 11). However, the yield of the desired product increased when the same reaction was conducted in a sealed tube, though the time required for the completion of the reaction increased to 10 h.

The present method was successfully extended for the synthesis of 2-substituted benzothiazoles **5** and 2-substituted benzoxazoles **7** from the reaction of 2-aminothiphenols **4** and 2-aminophenols **6**, respectively, with various β-diketones **2** (Scheme 3).

The reaction of 2-aminothiophenol **4a** with 2,4-pentanedione **2a** and 3,5-heptanedione **2b** gave the corresponding 2-methybenzothiazole **5a** and 2-ethylbezothiazole **5b** in excellent yield respectively (Table 3, entry 1–2). Also, the reaction of 2-aminophenol

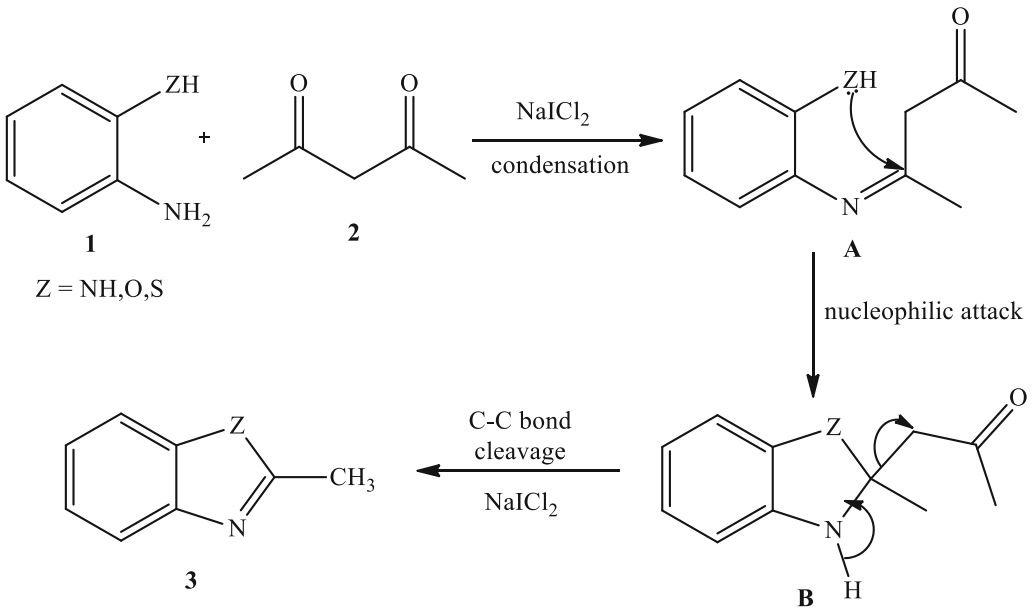


Scheme 4. Control experiments.

6a with 2,4-pentanedione **2a** gave the corresponding 2-methybenzoxazole **7a** in good yield (Table 3, entry 6). Next, the reactions of 4-chloro-2-aminothiphenol **4b**, 4-methyl-2-aminophenol **6b**, 4-chloro-2-aminophenol **6c** with β-diketones **2a** and **2b** smoothly proceeded to give corresponding benzothiazole and benzoxazole products in good to moderate yields (Table 3, entries 3, 4, 7, 8). From these results, it can be concluded that different substituent (either electron-donating group or electron-withdrawing group) on 2-aminothiophenol and 2-aminophenol had no significant impact on the reaction yield. Finally, the method was also successfully applied to the reaction of 2-aminothiophenol with unsymmetrical β-diketone, 1-methyl-3-phenyl-1,3-dione **2d**, the product 2-methylbenzothiazole was obtained in 57% yield (Table 3, entry 5). The reactions in which the yields were moderate, a polar side product was observed on TLC. This side product was isolated by column chromatography but could not be identified.

To gain insight into the mechanism, several control experiments were performed as depicted in Scheme 4. Initially, when *o*-phenylenediamine **1** was reacted with acetyl acetone **2** in presence of $NaICl_2$, the imine intermediate **A** (ketimine-enaminone tautomer) was observed [Scheme 4, (a)]. Further, when this imine was refluxed in THF in absence of $NaICl_2$ the corresponding 2-methy-1*H*-benzimidazole product **3** was not observed [Scheme 4, (b)]. However, the imine **A**, upon refluxing in THF in the presence of $NaICl_2$, gave the desired cyclised product 2-methy-1*H*-benzimidazole **3** [Scheme 4, (c)]. This finding supports the role of $NaICl_2$ in this cyclization and C-C bond cleavage reaction. However, the exact role of $NaICl_2$ in the pathway could not be determined as no other intermediates could be isolated in the reaction and very few literature reports are available to get a better insight into the mechanistic role of $NaICl_2$ as catalyst. Though, we suppose that $^{-}ICl_2$ forms a complex with the *N* of intermediates **A** and **B**, thus affording the intramolecular nucleophilic cyclization and subsequent C-C bond cleavage. Moreover, under the present reaction conditions, $NaICl_2$ did not cause iodination of *o*-phenylenediamine.

On the basis of the above experimental results as well as the literature reports, a plausible mechanism is proposed in Scheme 5. Initially, condensation reaction of *o*-phenylenediamine **1** with acetyl acetone **2** generates a ketimine intermediate **A**. The ketimine intermediate **A** undergoes an intramolecular nucleophilic addition to produce adduct **B**. The C-C bond cleavage reaction finally occurs to generate product **3**.



Scheme 5. Plausible Mechanism.

4. Conclusion

In conclusion, we have developed a general and facile route for the sodium dichloroiodate ($NaICl_2$) promoted synthesis of benzazoles by the condensation of *o*-amino anilines/thiophenols/phenols with β-diketone compounds through the C—C bond cleavage. The reaction can be performed with readily available starting material under mild conditions (without the use of strong oxidants, metal catalyst or Bronsted acid catalyst, and high temperature), and gives product with moderate to good yields and high purity.

Supplementary Information (SI)

General Information, Experimental details and ^{1}H and ^{13}C NMR spectra of selected synthesized compounds are accessible in Supplementary Information at www.ias.ac.in/chemsci.

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