Convenient and Robust Metal-Free Synthesis of Benzazole-2-Ones Through the Reaction of Aniline Derivatives and Sodium Cyanate in Aqueous Medium

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ABSTRACT: *Benzazole-2-one derivatives are of wide interest because of their diverse biological activities and clinical applications. Their core ring system is present in many drugs, pesticides, and pigments. Therefore, the development of novel and efficient methods for their synthesis is always interesting. In this article, we wish to report a novel, practical, and green synthesis of benzazole-2-ones by the reaction of aniline derivatives with sodium cyanate. Good to excellent yields of products have been obtained under metal- and ligand-free conditions in water as a solvent. This procedure avoids the use of time-consuming and tedious column chromatography and the products were easily isolated by simple extraction followed by washing with dichloromethane.*

KEYWORDS: *Benzazole-2-ones; Benzimidazolones, benzothiazolones; Benzoxazolones; Sodium cyanate; Green chemistry; Water; Synthesis.*

INTRODUCTION

Benzazole-2-ones (benzimidazolones, benzothiazolones, benzoxazolones) are important derivatives of benzazoles that exist widely in many biologically and pharmaceutically active molecules [1]. For example (Fig. 1), Pimozide **1** with brand name of Orap is an orally active antipsychotic drug marketed worldwide for the treatment of schizophrenia and other psychotic illnesses in adults [2]. Newer drug Flibanserin **2** (Addyi) is a multifunctional serotonin agonist and antagonist which is used for the treatment of pre-menopausal women with hypoactive sexual desire disorder [3]. Tiaramide **3** with trade name Solantal is an analgesic and anti-inflammatory medicine available in a number of countries worldwide [4]. The drug used for the treatment of different pain and inflammatory disorders. Chlorzoxazone **4** is a benzoxazolone derivative sold under the trade name

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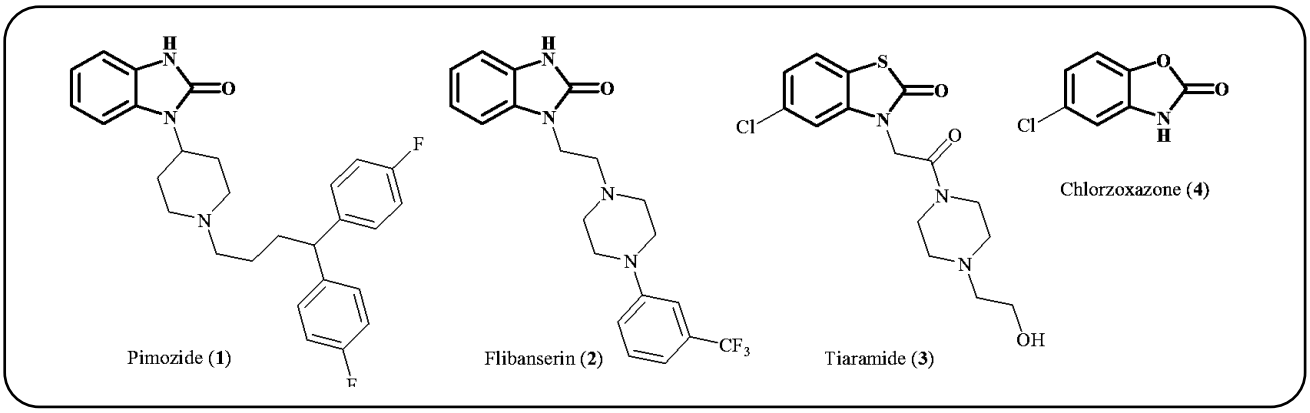


Fig. 1: Selected examples of drugs containing a benzazole-2-one core.

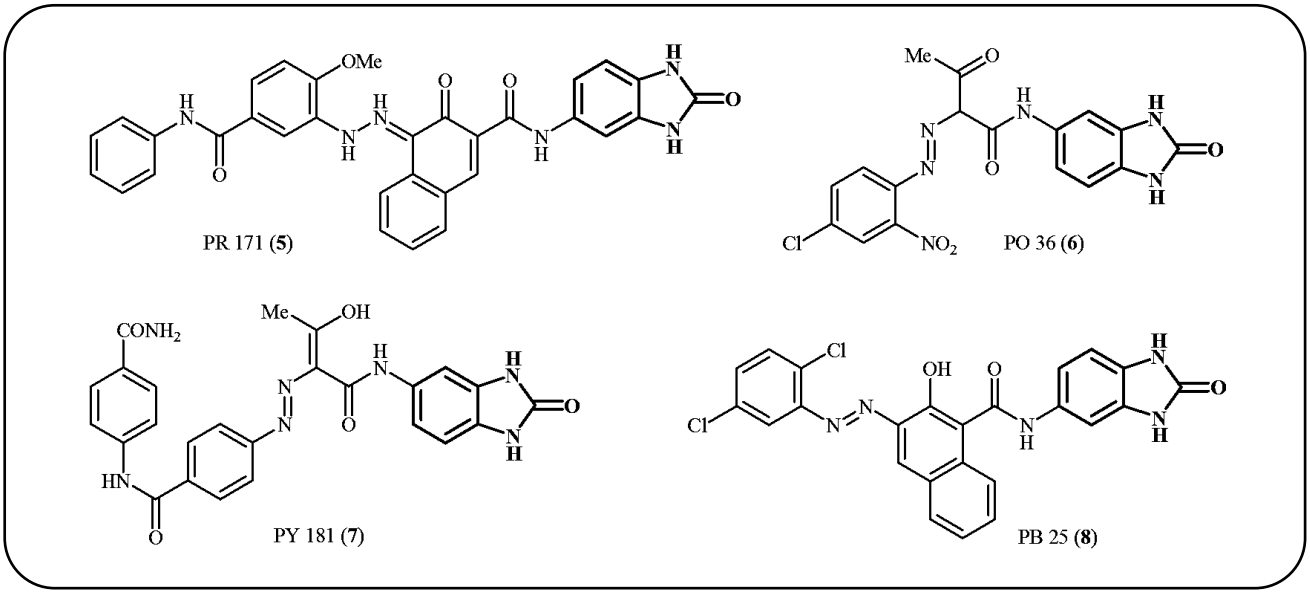
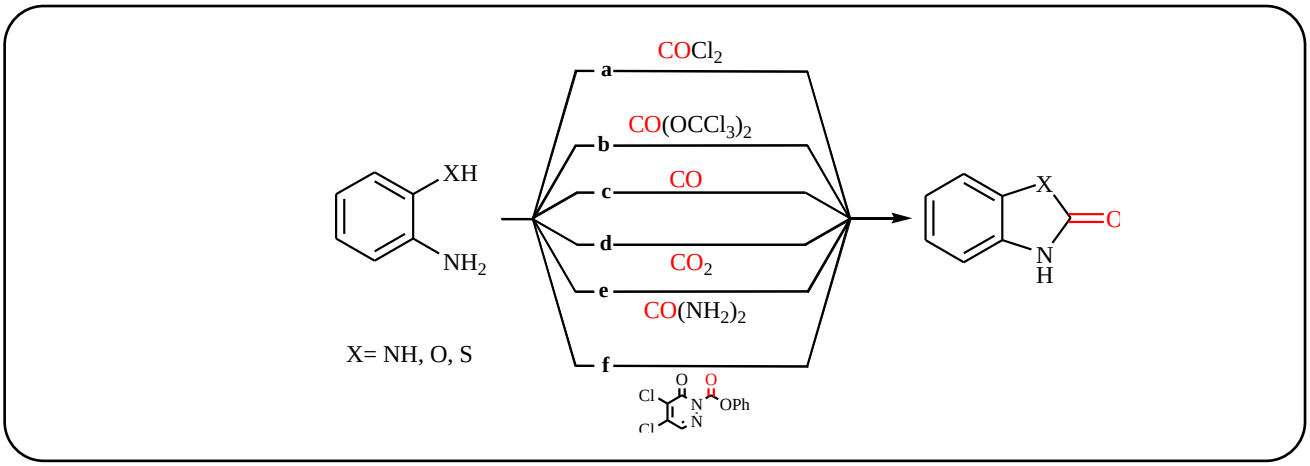


Fig. 2: Selected examples of pigments containing a benzimidazol-2-one core.

of Paraflex which is used to treat muscle spasms (pain). The drug works by blocking of pain sensations between the nerves and the brain [5]. Furthermore, benzazole-2-one derivatives also have many applications in agrochemical and material science [6]. For instance, benzimidazolones are one of the most important classes of synthetic organic pigments that are produced industrially on a large scale (Fig. 2). This class of pigments have excellent light and solvent fastness and widely used in printing ink, plastics, and industrial paint [7].

The traditional preparation of titled compounds mainly relies on the reaction of aniline derivatives (1,2-diaminobenzenes, 2-hydoxyanilines, and 2-mercaptoanilines) with highly toxic phosgene or triphosgene as C=O sources which may cause serious environmental pollution and safety problems (Scheme 1, route a, b) [8-10]. Over the past few years, several non-phosgene approaches have been reported, including condensation of corresponding anilines with C=O sources such as CO [11], CO_2 [12], and urea [13] (Scheme 1, route c-e). However, these methods often require a metal catalyst, gaseous acyl source, long reaction time, and/or high reaction temperature. Very recently, *Yoon* and *co-workers* reported the use of 2-phenoxycarbonyl-4,5-dichloropyridazin-3(2*H*)-one as a novel acyl source in this chemistry (Scheme 1, route f) [14]. However, this reagent is not commercially available and also releases large amounts of pyridazinone and phenol as waste. Thus,



Scheme 1: Synthetic route to benzazole-2-ones.

development of an efficient, convenient and economical protocol for the synthesis of benzazole-2-ones with green chemistry perspectives is still a significant issue.

In the context of our general interest in green chemistry [15] and following our research on the synthesis of heterocyclic compounds [16], herein, we propose a facile and environment friendly synthesis of benzazole-2-one derivatives through the reaction of non-toxic and commercially available anilines with sodium cyanate under metal- and ligand-free conditions in the most environmentally benign solvent, water.

EXPERIMENTAL SECTION

General

All the chemicals required for the synthesis of benzazole-2-ones were commercially available, obtained as highest purity reagents from Sigma-Aldrich (St. Louis, MO, USA), Fluka (Neu-Ulm, Germany) and Merck (Darmstadt, Germany) companies and were used as received. Analytical Thin-Layer Chromatography (TLC) was performed on Merck silica gel F-254 plates. Melting points were determined with a capillary apparatus and uncorrected. Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR) spectra were recorded using a Bruker Avance III 400 MHz spectrometer (Bruker, Billerica, MA, USA) in dimethyl sulfoxide (DMSO-d_6). Chemical shifts are reported in parts per million (ppm) and the coupling constants (*J*) are expressed in Hertz (Hz). Splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet; and dd, double of doubles.

General procedure for synthesis of benzazole-2-ones (10a–e, 12, 15)

To a solution of NaOCN (3 mmol) in 4 mL HCl (2M) was added aniline derivative (1.0 equiv.). The mixture was stirred at 90 °C for 24 h. The progress of the reaction was monitored by TLC (eluent: petroleum ether/ethyl acetate 2:1). After completion of the reaction, the mixture was cooled to room temperature and then extracted with EtOAc (3 × 5 mL). The organic phase was dried with Na_2SO_4 and the solvent was removed in vacuo. The oily residue was precipitated with CH_2Cl_2 to afford expected benzazole-2-ones as white powders.

Characterization of benzazole-2-ones (10a–e, 12, 15)

Benzo[d]imidazol-2(3H)-one (10a)

Yield: 91%; mp 316-319 °C (lit.[17] 320-322). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, TMS): δ = 6.93 (s, 4 H), 10.59 (s, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K, TMS): δ = 109.04, 120.97, 130.34, 155.99.

5-Methyl-1H-benzo[d]imidazol-2(3H)-one (10b)

Yield: 86%; mp 298-300 °C (lit.[17] 295-297). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, TMS): δ = 2.28 (s, 3 H), 6.73 (d, *J*= 7.2 Hz 2 H), 6.80 (d, *J*= 7.2 Hz, 1 H), 10.46 (d, *J*= 15.2 Hz, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K, TMS): δ = 21.49, 108.62, 109.47, 121.34, 127.91, 129.81, 130.31, 155.89.

5-Chloro-1H-benzo[d]imidazol-2(3H)-one (10c)

Yield: 79%; mp 323-327 °C (lit.[17] 324-326). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K, TMS) δ 6.98-6.89 (m, 3H),

10.76 (s, 2H); 13C NMR (75 MHz, DMSO-d_6, 298 K, TMS) δ 108.48, 109.55, 120.17, 124.56, 128.69, 130.87, 155.21 [17].

5-Fluoro-1H-benzo[d]imidazol-2(3H)-one (10d)

Yield: 72%; mp 300-302 °C (lit.[17] 300). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K, TMS) δ 6.81 (m, 3H), 10.65 (s, 1H), 10.76 (s, 1H); 13C NMR (75 MHz, DMSO-d_6, 298 K, TMS) δ 106.36, 108.88, 117.85, 126.01, 130.029, 130.48, 155.71 [17].

4-Methyl-1H-benzo[d]imidazol-2(3H)-one (10e)

Yyield: 81%; mp 296-299 °C (lit.[18] 297-300). ^{1}H NMR (270 MHz, DMSO-d_6, 298 K, TMS): δ = 2.25 (s, 3 H), 6.85-6.71 (m, 3 H), 10.53 (s, 1 H), 10.65 (s, 1 H). ^{13}C NMR (67.8 MHz, DMSO-d_6, 298 K, TMS): δ = 16.1, 106.0, 118.1, 120.3, 121.5, 128.5, 129.2, 155.5 [19].

Benzo[d]thiazol-2(3H)-one (12)

Yield: 88%; mp 138-139 °C (lit.[17] 138-139). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, TMS): δ = 7.11-7.57 (m, 4 H), 11.89 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K, TMS): δ = 111.95, 123.05, 123.14, 123.78, 126.86, 136.80, 170.59.

4-Hydroxy-1H-benzo[d]imidazol-2(3H)-one (12)

Yield: 76%. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, TMS): δ = 6.40 (d, *J*= 7.6, 1 H), 6.78 (d, *J*= 8, 1 H), 7.01 (s, 1 H), 7.06 (t, *J*= 8, 1 H), 8.49 (s, 1 H), 9.34 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K, TMS): δ = 105.59, 109.27, 109.39, 129.92, 141.25, 152.72, 158.21.

RESULTS AND DISCUSSION

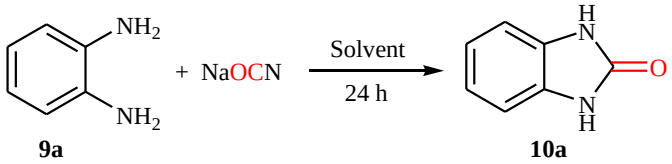
We started our investigation with benzene-1,2-diamine. The reaction of 1 equiv of benzene-1,2-diamine **9a** with NaOCN was selected as a model reaction to screen the experimental conditions. Selected results are summarized in Table 1. Firstly, the reaction was carried out in methanol at room temperature under an air atmosphere. However, no product was observed after 24 h (Table 1, entry 1). Performing the reaction under reflux conditions gave identical results (Table 1, entry 2). Likewise, when ethanol was used as solvent, the reaction failed to give any desired product (Table 1, entries 3, 4) but in the presence of binary solvent ethanol/water with ratio 1:1, a very low yield was noticed (Table 1, entry 5). It is pleasing to observe that addition of some drop of HCl to the reaction mixture afforded a 32% yield of expected product **10a** (Table 1, entry 6). The results encouraged us to further explore and optimize the conditions. Interestingly, the yield of **10a** increased from 32% to 49% when the reaction was carried out in 1 M HCl solution at room temperature (Table 1, entry 7). At 90 °C, formation of the imidazolone increased and the desired product was isolated in 78% yield (Table 1, entry 8). When the reaction was carried out in 2 M HCl solution, the yield significantly increased up to 93% (Table 1, entry 9). Continuing to increase the pH did not lead to an increase of the yield of **10a** (Table 1, entry 10). Thus, the optimal reaction conditions were determined to be HCl (2 M) as the solvent at 90 °C for 24 hours.

To explore the scope of the reaction, a variety of 1,2-diaminobenzenes was used (Table 2). Generally, the cyclization proceeded smoothly to afford the corresponding benzimidazolones in high to excellent yields under the optimized conditions [17]. Interestingly, the electronic character of the substituents in the phenyl ring periphery of 1,2-diaminobenzenes had a little effect on the rate of the reaction, as both electron-rich and electron-deficient substrates reacted efficiently. Furthermore, the reaction was successfully performed on a gram scale to give isolated yields comparable to those obtained from small-scale reactions (Scheme 2).

Inspired by the above results, we next briefly turned our attention to extend this procedure to the synthesis of benzothiazolones and benzoxazolones starting from 2-mercaptoanilines and 2-hydoxyanilines, respectively. Pleasingly, the protocol was found to work well when 2-aminothiophenol **11** was employed as the substrate. The corresponding product **12** was isolated in 88% yield (Scheme 3a). Surprisingly, the synthesis of benzoxazolone **14** *via* the reaction of 2-aminophenol **13** with NaOCN under the optimized conditions was hampered due to the unexpected formation of 4-hydroxy-benzimidazolone **15** in 76% yield as the sole product (Scheme 3b).

Finally, the analogous conditions was used to obtain mono cyclic azolidin-2-ones (imidazolidin-2-one, thiazolidin-2-one, and oxazolidin-2-one). However, the reaction between NaOCN and ethane-1,2-diamine, 2-aminoethanethiol, and 2-aminoethanol were unsuccessful and the corresponding urea derivatives were obtained as the sole products (Scheme 4).

Table 1: Optimization of the conditions for the model reaction of benzene-1,2-diamine 9a with NaOCN[a]

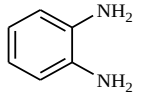
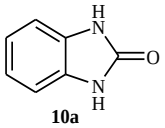
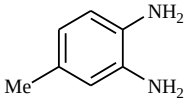
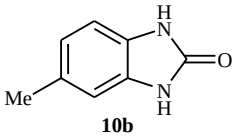
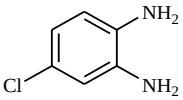
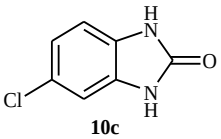
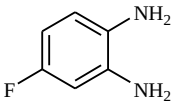
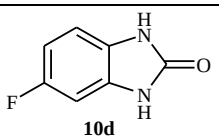
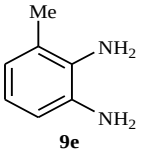
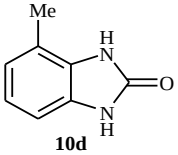


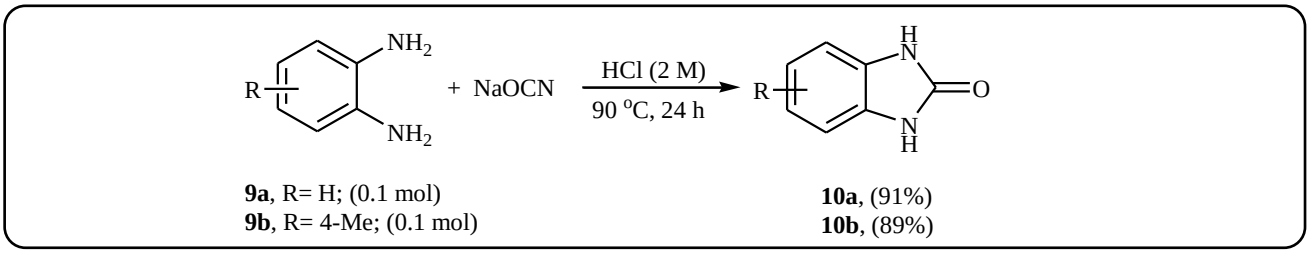
9a **10a**

Entry	Solvent	Temperature (°C)	Yield (%)[b]
1	MeOH	25	NR[c]
2	MeOH	reflux	NR
3	EtOH	25	NR
4	EtOH	reflux	NR
5	EtOH/H_2O	25	trace
6[d]	EtOH/H_2O	25	32
7	HCl (1 M)	25	49
8	HCl (1 M)	90	78
9	HCl (2 M)	90	93
10	HCl (3 M)	90	87

a) Reaction conditions: NaOCN (3.0 mmol, 1.0 equiv.), aniline (1.0 equiv.), solvent (4 mL).
b) Isolated yields. [c]No reaction. [d]Some drop of HCl were added to the reaction mixture.

Table 2: Synthesis of benzimidazolones 10a-e by reaction of 1,2-diaminobenzenes 9a-e with NaOCN in water.

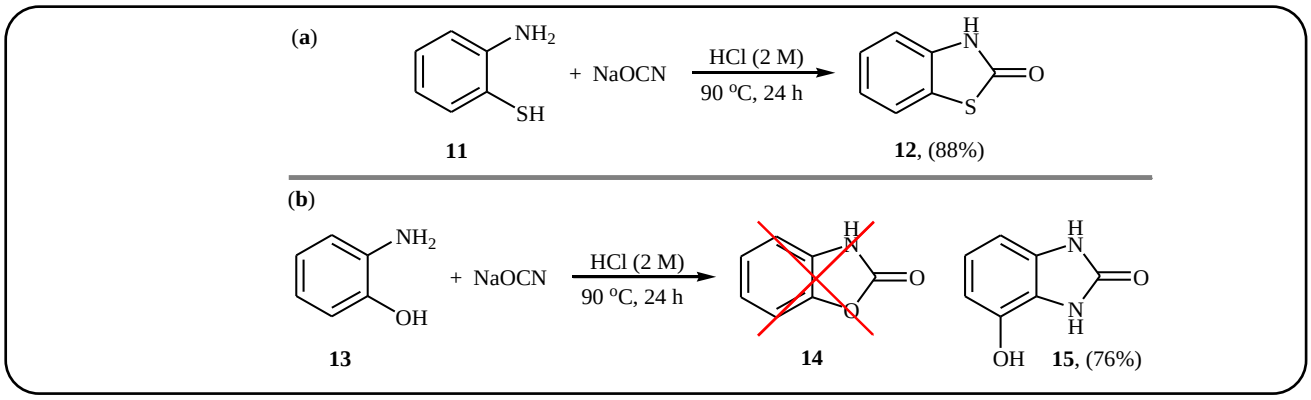
Entry	Substrate	Product	Yield (%)
1	 **9a**	 **10a**	93
2	 **9b**	 **10b**	86
3	 **9c**	 **10c**	79
4	 **9d**	 **10d**	72
5	 **9e**	 **10d**	81



9a, R= H; (0.1 mol)
9b, R= 4-Me; (0.1 mol)

10a, (91%)
10b, (89%)

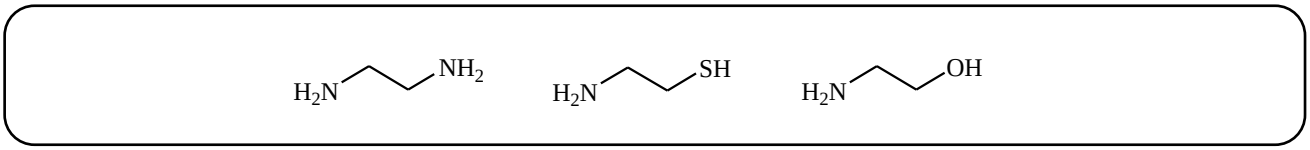
Scheme 2: Gram-scale reaction of 9a and 9b with NaOCN.



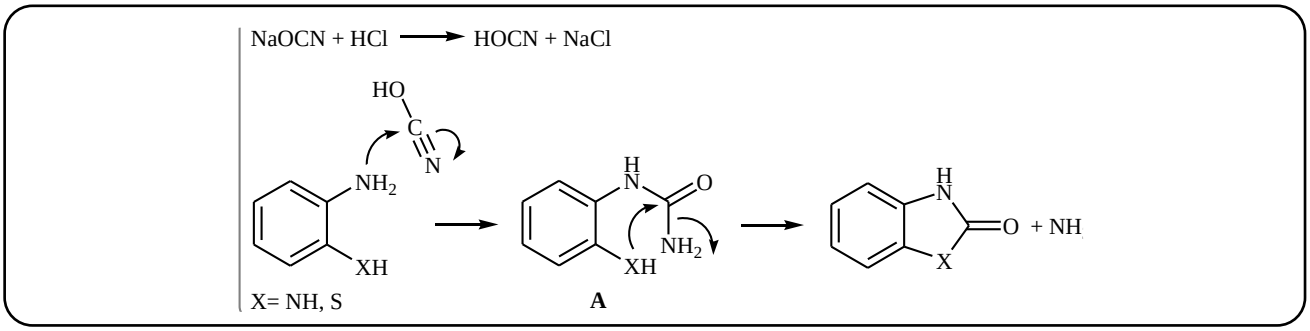
11 **12**, (88%)

13 **14** **15**, (76%)

Scheme 3: (a) Synthesis of benzothiazolone 12; (b) Attempted synthesis of benzoxazolone 14 results in unexpected hydroxy substituted benzimidazolone 15.



Scheme 4: Chemical structures of aliphatic amines used.



Scheme 5: A proposed mechanism for the formation of benzazole-2-ones.

A mechanism for this transformation is proposed n Scheme 5. The reaction proceeds by generation of a urea intermediate **A** by nucleophilic addition of amino group of aniline to the carbon atom of *in situ* generated cyanic acid (HOCN). Intermediate **A** then undergoes intramolecular nucleophilic addition to give the corresponding benzazole-2-one and one molecule of ammonia. The detailed mechanistic studies for the reaction of 2-aminophenole and NaOCN are currently under investigation.

CONCLUSIONS

In summary, a straightforward, green and environmentally friendly protocol has been initially developed for the synthesis of benzazole-2-ones *via* metal-

free reaction of aniline derivatives with sodium cyanate. A series of potential biological benzimidazolone and benzothiazolone frameworks could be conveniently obtained in good to excellent yields even in gram scale. This novel procedure can enjoy the following advantages: (a) low-cost commercially available and non-toxic NaOCN as the carbonylating agent; (b) water as solvent; (c) easy workup procedure; (d) no addition of any catalyst or ligand; (e) high product yields. Further investigations of the substrate scope of this method and the reaction mechanism are currently in progress in our laboratory.

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