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DBUHI3 complex an efficient catalyst for the synthesis of 2-phenylbenzimidazole and benzothiazole derivatives

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Abstract: Herein, we have reported the facile synthesis of various benzimidazole/benzothiazole by using DBU–iodine–iodide as a green and simple catalyst. The R3NHI3 complexes have been formed by reacting an aqueous mixture of ammonium iodide and molecular iodine with the aqueous solution of amine. The structure of R3NHI3 complexes has been confirmed by spectroscopic techniques. The prepared amine–iodine complexes were screened as a catalysts in the synthesis of benzimidazole/benzothiazoles. Among the screened catalysts DBUHI3 complex has been found as most efficient catalyst. The synthesis of benzimidazoles and benzothiazoles has been achieved with the reaction of *o*-phenylene diamine/*o*-aminothiophenol and various substituted aryl aldehyde using DBUHI3 as a catalyst. The present protocol has offered some advantages over other reported protocols such as the mild reaction condition, commercially available precursors, inexpensive catalyst, short reaction time, the broad scope of the substrate, high yield, simple isolation of the product and environmentally benign method.

Keywords: amine–iodine complexes; benzimidazole; benzothiazole; oxidative cyclization; organocatalysis.

INTRODUCTION

Benzimidazoles and benzothiazoles are valuable heterocyclic scaffolds due to their many applications in diverse fields such as agrochemicals, veterinary, and pharmaceuticals.[1–3] They are potent privileged bicyclic aromatic nuclei in organic and medicinal chemistry. They showed diverse biological activity.[4–7] Benzimidazole and benzothiazole are the core structural skeleton in a variety of drug molecules specifically pantoprazole, riluzole, clemizole, bendamustine, thiabendazole, telmisartan, benzitramide, omeprazole, Hoechst 33342, pimoben-

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dan, mibefradil, dovitinib EGFR-3, sulfathiazole, ritonavir, abafungin, tiazofurin and benazolin. This class of heterocyclic compounds display valuable properties like photochromic, biochemical luminescence, and solvatochromic properties.[8,9] These heterocyclic molecules have significant biological activity and great pharmaceutical potential to attract more attention from synthetic chemists (Fig. 1).

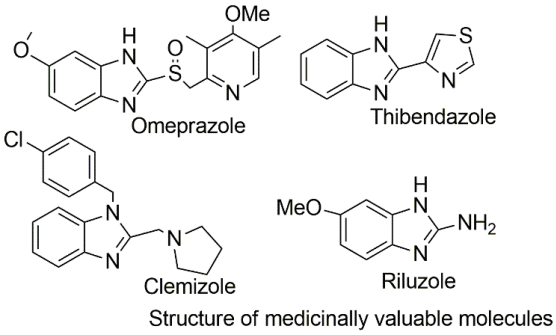


Fig. 1. Benzimidazoles ring containg drug molecules.

The robust method for synthesis of these molecules involves the treatment of *o*-phenylenediamine[10] and 2-aminothiophenol[11] with carbonyl compounds, such as aldehyde using Bronsted or Lewis acid catalyst[12] and carboxylic acids[13] or their derivative (nitrile, amide, ester, acid chloride)[14] at elevated temperature. Another approach involves metal-catalyzed direct alkylation of these molecules *via* C–H activation followed by carbon–carbon bond formation.[15] Synthesis of these molecules was achieved by microwave,[16] ultrasonic wave,[17] ionic liquid,[18] ionic liquid gel,[19] nanomaterial,[20] DMF[21] and under oxidative condition using various oxidative and catalytic reagents cited in the reference.[22,23] The certain green synthesis of benzimidazole was accomplished by homogeneous catalysis such as use of triflate erbium catalyst,[24] use of active deep eutectic solvent[25] and montmorillonite K 10 heterogenous green catalyst.[26] Generally, nearly all methods of benzimidazole synthesis have worked for benzothiazole.[27] The reported methods have limitations such as harsh reaction conditions, poor yield, high temperature, hazardous and carcinogenic solvent, expensive catalyst, side reaction, slow reaction rate, toxic reagents or tedious workup procedure and difficulty to isolate the product from the reaction mixture. Consequently, a search for better catalyst and environmentally benign methodology has continued for the economy and operational simplicity. Our catalytic procedure for amine–iodine complex is overcoming these problems.

Iodine catalysis has been known for more than 100 years. It has remarkably catalyzed various types of reactions.[28,29] The drawback of molecular iodine catalyzed synthesis of 2-substituted benzimidazole and benzothiazole is the sub-

limation of molecular iodine and moisture sensitivity, we have overcome these problems with amine-iodine-iodide complex organocatalyst.

We have synthesized the new R3NHI3 complexes using amine, ammonium iodide and molecular iodine.[30] The R3NHI3 complexes were characterized by spectroscopic technique and confirmed.[31] These catalysts were air-stable, and iodine never sublimates or deliquescent. Amine–iodine complex catalyzes the synthesis of 2-aryl benzimidazole and benzothiazole, also offers several advantages namely short reaction time, easy workup procedure and environmentally benign protocol. Amine–iodine complexes are organocatalysts that have an indispensable part in synthetic green chemistry because they are stable, less expensive, less toxic and easily applicable to a wide range of substrates. Herein, we have reported amine–iodine complexes catalyzed condensation and cyclization of a wide variety of aryl aldehyde with *o*-phenylenediamine and *o*-aminothiophenol, respectively. Moreover, we described the synthesis of new amine–iodine complexes (**1a**–**e**) and their synthetic application.

EXPERIMENTAL

The commercially available chemical reagents and solvents were used and their purity was ensured before use. Solvents that were entirely dry and free of impurities were used. Reaction of the progress was checked on Merck TLC silica gel 60 F254 plates using UV lamp (365 and 254 nm) and iodine chamber. The melting point was determined using open capillary method. The recorded melting points were uncorrected. PerkinElmer FTIR spectrometer was used to record IR spectra. Bruker Avance III HD NMR 500 MHz spectrometer was used to obtained ^{1}H-NMR and ^{13}C-NMR spectra in DMSO-d_6 and $CDCl_3$. HRMS analysis was obtained on a Bruker Impact II UHR-TOF mass spectrometer system.

Preparation of DBU–Iodine complexes

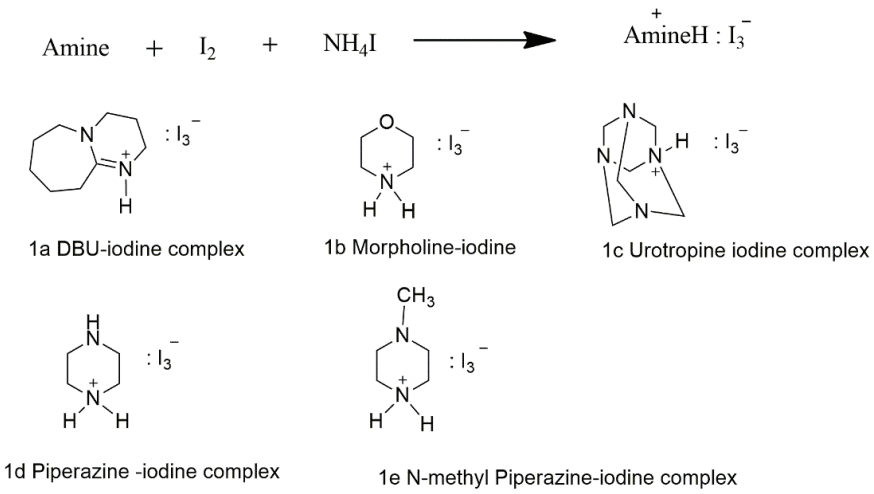
2.665 g of Ammonium iodide (18.352 mmol, 2.8 eq.) was added to 5.2 mL water (2 volumes) to get a clear solution in a 250 mL beaker, followed by the addition of 1.667 g of iodine (6.568 mmol, 1 eq). This solution was added dropwise to a stirred solution of 1 g DBU (6.568 mmol, 1 eq) in 8 mL water (8 volumes) in a 250 mL round bottom flask. The solid product has formed during addition, the mixture stirred for 15 min, and the solid product filtered off. The product has been washed with cold water and dried under a vacuum to provide the desired complexes. After drying the complex, the yield has been reported.

Typical process for the synthesis of benzimidazole/benzothiazole from o*-phenylenediamine/thiophenol and aldehyde*

A mixture of *o*-phenylenediamine/*o*-aminothiophenol (1 mmol) and aryl aldehydes (1 mmol) was dissolved in 2 mL ethanol in a 25 mL round bottom flask. The catalyst DBUH+I_3 complex **1a** (15 mol %) added to the reaction mixture, and the reaction mixture was stirred for 30 min. The progress of the reaction was monitored by (hexane:ethyl acetate) TLC. After completion of the reaction, the solvent evaporated under a vacuum. The crude reaction mixture was quenched with 20 % sodium thiosulfate solution. The product was isolated by extracting with ethyl acetate. The organic layer was dried over sodium sulfate and purified by column chromatography. The structure of the compound was confirmed by the spectroscopic techniques and matched with the reported.

RESULTS AND DISCUSSION

We have prepared a series of R3NHI3 complexes (**1a**–**e**), with minor modification in the reported procedure,[27,28] by replacing potassium iodide with ammonium iodide. This change has led to a drastic change in the structure and composition of catalysts. In the previous reported procedure by Livia *et al.*[72] a precipitate of the complex with composition $R_2NH:I_2:KI$ has formed. In the present work, we have got a composition as R3NHI3 (Scheme 1). Amine must contain two heteroatoms in the cyclic system for precipitation and stability of the complex. The amines like pyrrolidine, piperidine and amino acid proline did not form solid complexes by the same procedure as a result of a single nitrogen atom in the cyclic structure.



Scheme 1. Synthesis of amine-H–I_3 complex and structure of respective complex.

The various amine–iodine–iodide complexes have been prepared using easily available amine, ammonium iodide and molecular iodine. The molecular iodine was dissolved in the aqueous solution of ammonium iodide then added to an aqueous solution of amine dropwise, amine–iodine–iodide complex precipitated out and respective amine was obtained (Table I). The product was washed with excess water till filtrate was free from ammonia, confirmed by moist turmeric paper.

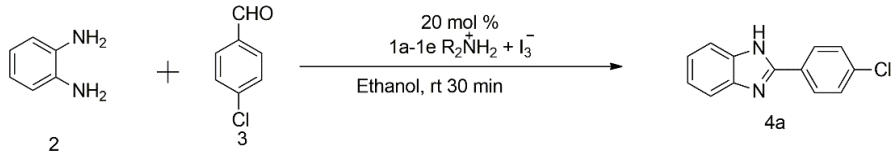
The structure of synthesized amine-iodine complexes (**1a-1e**) was confirmed by spectroscopic techniques such as UV, IR, HRMS, EDS, ^{1}H- and ^{13}C-NMR. These new homogenous catalysts were screened for the synthesis of 2-aryl benzimidazole. We have chosen ethanol as a solvent for screening catalytic activity of the amine-iodine complex catalyst because they are freely soluble in ethanol and partly soluble in various other organic solvents.

TABLE I. Synthesis of R3NHI3 complexes; amine (6.568, 1 eq.), iodine (6.568 mmol, 1 eq.) and ammonium iodide (18.352 mmol, 2.5 eq.) in 2 mL water

No.	Complex	Color	Yield[a], %
1	DBU-H+I_3 complex	Greenish yellow	92
2	Morpholine-H+I_3 complex	Orange yellow	62
3	Urotropine-H+I_3 complex	Brown yellow	58
4	Piperazine-H+I_3 complexes	Dark brown yellow	73
5	*N*-methyl piperazine-H+I_3 complexes	Pinkish yellow	66s

[a]Isolated yield after purification

Initially, our studies were with the screening of prepared amine iodine complexes (**1a**–**e**) for synthesis of benzimidazole *via* condensation and cyclization reaction of commercially available *o*-phenylenediamines with *p*-chorobenzaldehyde (Scheme 2). The DBUHI3 complex has given high yield of 2-(4-chlorophenyl)-*1H*-benzimidazole and the results are in Table II.



Scheme 2. Model reaction for screening of R_2NH_2+I_3 complex for synthesis of benzimidazole.

TABLE II. Screening of R3NHI3 complex catalyst in the synthesis of 2-(4-chlorophenyl)-1*H*--benzimidazole (**4a**); reaction conditions: *o*-phenylenediamine (1 mmol), *p*-chlorobenzaldehyde (1 mmol), R3NHI3 complexes **1a**–**e** (20 mol %) in ethanol (2 mL) at room temperature for 30 min

Sr. No.	Complex	Yield[a], %
1	DBUH+I_3 complex	91
2	Morpholine-H+I_3complex	74
3	Urotropine-H+I_3 complex	85
4	Piperazine-H+I_3 complexes	80
5	*N*-Methylpiperazine-H+I_3 complexes	78
6	Iodine	70
7	Without catalyst	Trace

[a]Isolated yield after purification

Next, we have decided to optimize the amount of DBUHI3 complex with the same reaction condition. The amount of DBUHI3 was optimized by increasing the amount from 5 to 20 mol % for 1 mmol scale reaction. When the reaction was performed in the absence of the catalyst, the product has formed in a trace amount (Table III, entry 1). The yield has increased with the mol % of amine––iodine complex (Table III, entries 2–5). Nevertheless, there was no increase in the yield when the amount of R3NHI3 catalyst loading has increased from 15 to

20 % mol. From Table III was observed that the 15 mol % of DBUHI3 complex was sufficient to achieve excellent yield.

TABLE III. Optimizing the amount of DBUH+I_3 complex in synthesis of 2-(4-chlorophenyl)--1*H*-benzimidazole (**4a**); reaction conditions: *o*-phenylenediamine (1 mmol), *p*-chlorobenzaldehyde (1 mmol), DBUHI3 complex **1a** in ethanol (2 mL) at room temperature for 30 min

Entry	Catalyst quantity, mol %	Yield[a], %
1	Without catalyst	Trace
2	5	65
3	10	80
4	15	91
5	20	91

[a]Isolated yield after purification

We have studied the effect of various solvents on product yield (Table IV, entries 1–9). Among the screened solvents ethanol, toluene, and chloroform have given excellent yield, and ethanol was found the best solvent for the reaction as a high amount of product was obtained. Second, fortunately the choice of ethanol also falls on the fact that it is less toxic and more eco-sustainable solvent than chloroform and toluene. Hence, we have selected the solvent for the synthesis of benzimidazole. The solvents DMF, DMSO and acetonitrile offered a moderate product yield.

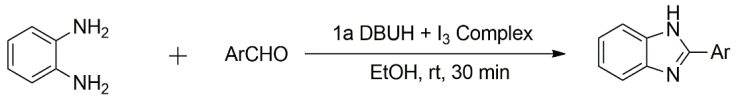
TABLE IV. Effect of solvent in synthesis of 2-(4-chlorophenyl)-1*H*-benzimidazole (**4a**) using DBUH–I_3 complex catalyst; reaction conditions: *o*-phenylenediamine (1 mmol), *p*-chlorobenzaldehyde (1 mmol), DBUHI3 complex **1a** (15 mol %) in ethanol (2 mL) at room temperature for 30 min

Entry	Name of solvent	Yield[a], %
1	Ethanol	91
2	Toluene	86
3	Dimethyl formamide	58
4	Dimethyl sulphoxide	66
5	Chloroform	80
6	Acetic acid	50
7	Acetonitrile	61
8	Tetrahydrofuran	31
9	Water	25

[a]Isolated yield after purification

With the investigated optimum reaction condition, we have synthesized various substituted benzimidazole (Scheme 3). The 2-aryl substituted benzimidazole have been synthesized from *o*-phenylenediamine (1mmol) with several substituted aryl aldehyde (1 mmol) *via* condensation and cyclization reaction in the presence of DBUHI3 complex (15 mol %) at room temperature in ethanol (Table V). It was found that various substituted aryl aldehyde containing electron-

donating groups (*p*-halogen and methoxy (Table V, entries 1, 4, 5 and 16) and electron-withdrawing group (nitro, Table V, entries 2, 6 and 14) were formed the product with good yield, under optimized condition. The heterocyclic aromatic aldehyde (Table V, entries 10a and 13a) gave a comparatively lower yield under the same condition. Hydroxy benzaldehyde (Table V, entries 11 and 12) has afforded an unexpectedly low yield, which may be due to solubility in water. The aryl aldehyde bearing electron-withdrawing at ortho/para nitro group (Table V, entries 13 and 15) has afforded product in poor yield. The *o*-substituted aryl aldehyde (Table V, entries 3, 12 and 15) has afforded a low yield due to steric hindrance in cyclization.



2 3 4a-v

Scheme 3. DBU–iodine–iodide catalyzed synthesis of substituted benzimidazole.

TABLE V. Synthesis of 2-aryl substituted benzimidazole; reaction conditions: *o*-phenylenediamine (1 mmol), substituted arylaldehyde (1 mmol), DBUHI3 complex **1a** (15 mol %), EtOH 2 ml, 30 min at rt

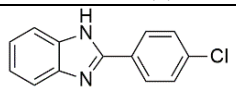
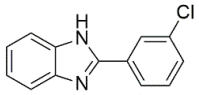
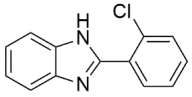
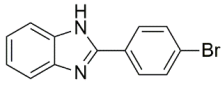
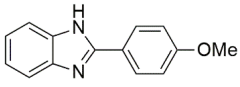
Entry	Product (**4**)	Yield[a], %	M. P., °C	Literature M. P., °C
1	 **4a**	91[c]	290–293	290–292[29]
2	 **4b**	86[c]	228–230	227–229[20]
3	 **4c**	73[e]	232–234	231–233[29]
4	 **4d**	78[d]	286–290	292–293[29]
5	 **4e**	76[d]	223–225	222–223[30]

TABLE V. Continued

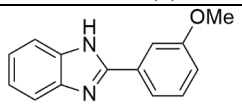
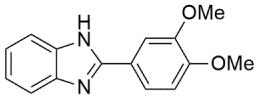
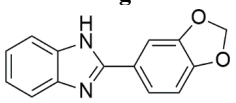
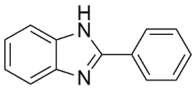
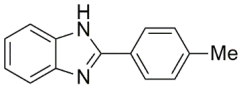
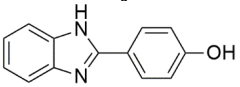
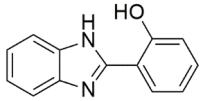
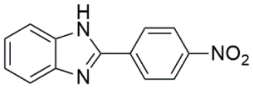
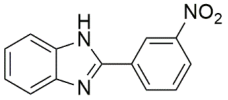
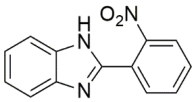
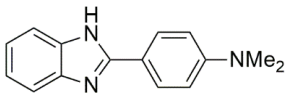
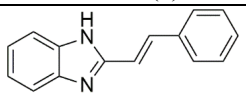
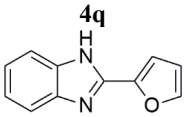
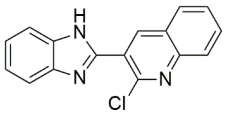
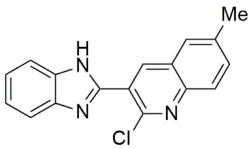
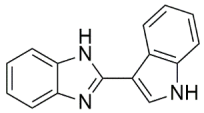
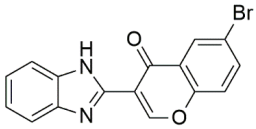
Entry	Product (**4**)	Yield[a], %	M. P., °C	Literature M. P., °C
6	 **4f**	81[c]	202–205	200–202[29]
7	 **4g**	64[d]	225–227	223–226[31]
8	 **4h**	72[d]	238–240	239–241[30]
9	 **4i**	80[c]	243–245	242–244[20]
10	 **4j**	65[d]	216–219	214–216[20]
11	 **4k**	80[c]	252–254	254–255[29]
12	 **4l**	44[c]	204–206	205–206[31]
13	 **4m**	41[d]	301–303	300[18]
14	 **4n**	72[c]	196–198	199[18]
15	 **4o**	38[c]	229–231	230[18]
16	 **4p**	72[d]	280–283	277–279[29]

TABLE V. Continued

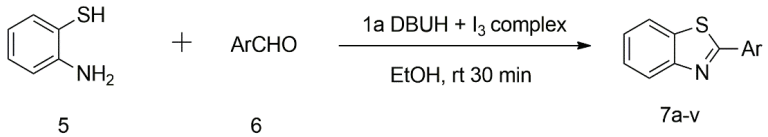
Entry	Product (**4**)	Yield[a], %	M. P., °C	Literature M. P., °C
17	 **4q**	51[f]	270–273	164–166[20]
18	 **4r**	68[d]	226–228	221–223[20]
19	 **4s**	63[d]	219–222	202[32]
20	 **4t**	73[d]	221–224	220[33]
21	 **4u**	72[f]	220–223	226–227[23]
22	 **4v**	76[e]	269–271	–

[a]Isolated yield after purification; [b]product was purified by recrystallization in ethanol; [c]product was purified by column chromatography mobile phase hexane: ethyl acetate; [d]product was purified by recrystallization in chloroform; [e]product was purified by column chromatography mobile phase chloroform

Thus, the R3NHI3 complex was catalyzing the synthesis of 2-aryl substituted benzimidazole using a diverse range of aryl aldehydes and *o*-phenylenediamine. All synthesized benzimidazole derivatives were characterized by ^{1}H-, ^{13}C-NMR and physical constants compared with standard data. The ^{1}H-NMR displays a characteristic nitrogen-bearing proton chemical shift δ value 12.5–13.5 ppm that reflected in each derivative, whereas the ^{13}C-NMR show a typical chemical shift δ value 150 ppm for carbon located between two nitrogens (Supplementary material to this paper).

The synthesis of 2-substituted aryl benzothiazole derivative (Scheme 4) was achieved from 2-aminothiophenol and diversity of aryl aldehydes in the presence of DBUHI3 complex **1a**. The aromatic aldehyde bearing electron-donating group

(*p*-halogen, methoxy, hydroxyl, amino (Table VI, entries 1, 4, 5, 8, 11, 12, 13, and 17)) and electron-withdrawing group (*m*-halogen, methoxy, nitro group, Table VI, entries 2, 6 and 14–16) provided a good yield of the product under same optimized process. Also, this reaction works well with the heterocyclic aromatic aldehyde to form a product **7** in moderate yield (Table VI, entries 19––22). The *o*-substituted benzaldehyde has afforded a poor yield of the product because of a steric hindrance (Table VI, entry 3). The unexpectedly *o*-nitro benzaldehyde has afforded a product in the higher yield owing to the high polarity of aldehyde (Table VI, entry 16). Overall, the amine–iodine complex has remarkably catalyzed the synthesis of 2-substituted aryl benzothiazole derivatives. The structure of all synthesized compounds were confirmed by NMR spectroscopic data and physical constants compared with standard data. The ^{13}C NMR spectra of benzothiazole have shown a characteristic value of chemical shift δ 168 ppm for carbon between two heteroatoms sulfur and nitrogen (Supplementary material).



Scheme 4. DBUHI3 catalysed synthesis of benzothiazole derivatives.

TABLE VI. Synthesis of 2-aryl substituted benzothiazole; reaction conditions: *o*-aminothiophenol (1 mmol), substituted arylaldehyde (1 mmol), DBUHI3 complex **1a** (15 mol %), ethanol 2 mL, 30 min at rt

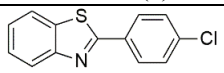
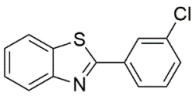
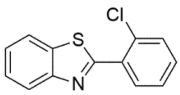
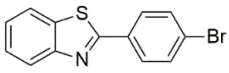
Entry	Product (**7**)	Yield[a], %	M. P., °C	Literature M. P., °C
1	 **7a**	84[d]	115–117	111–112[31]
2	 **7b**	72[c]	94–95	93–94[31]
3	 **7c**	58[d]	80–82	83–84[31]
4	 **7d**	80[c]	127–129	129–131[33]

TABLE VI. Continued

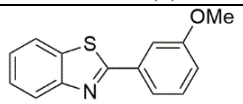
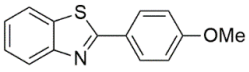
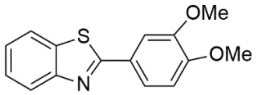
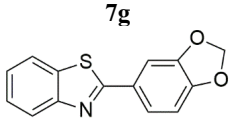
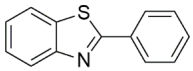
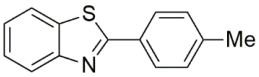
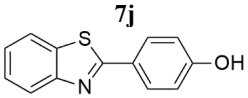
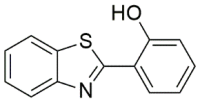
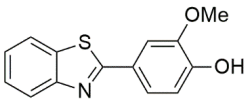
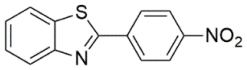
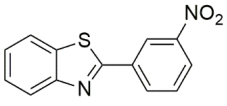
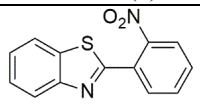
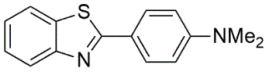
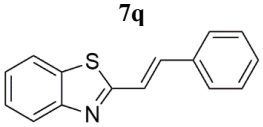
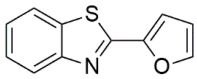
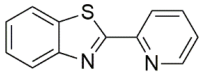
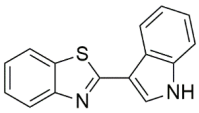
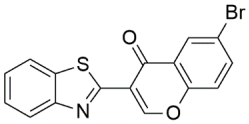
Entry	Product (**7**)	Yield[a], %	M. P., °C	Literature M. P., °C
5	 **7e**	74[c]	120–121	120–122[34]
6	 7f	64[d]	99–102	98–100[35]
7	 **7g**	61[f]	229–231	230–232[36]
8	 **7h**	83[d]	130–132	128–130[37]
9	 **7i**	91[d]	112–113	109–110[33]
10	 **7j**	62[e]	85–86	87–88[38]
11	 **7k**	79[c]	227–229	225–227[39]
12	 **7l**	86[c]	131–132	124–126[39]
13	 **7m**	83[c]	160–162	161–163[39]
14	 **7n**	82[e]	320–322	228–230[39]
15	 **7o**	78[e]	190–193	185–187[36]

TABLE VI. Continued

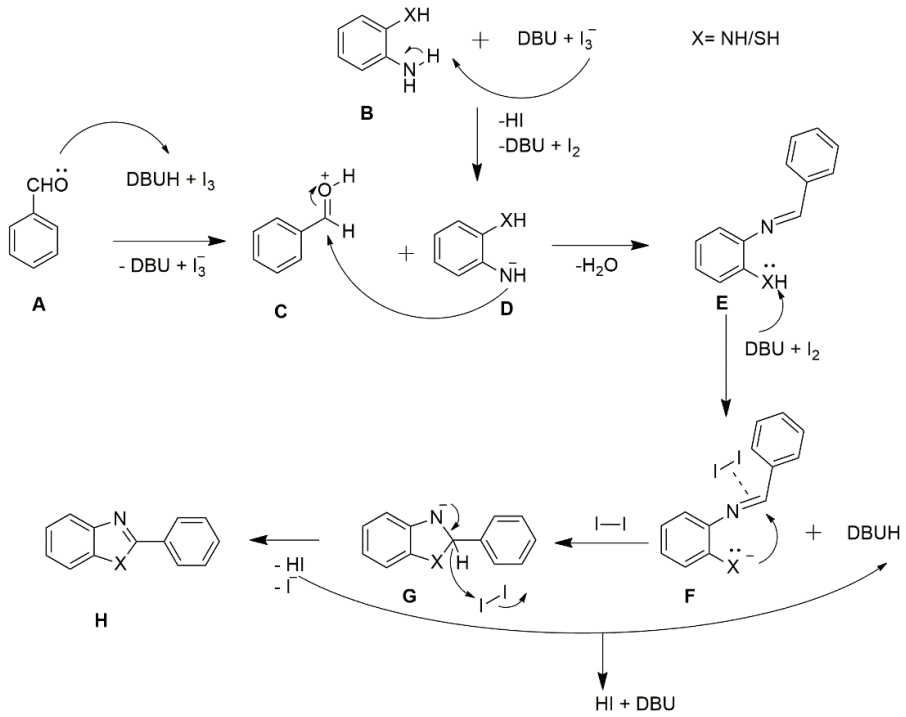
Entry	Product (**7**)	Yield[a], %	M. P., °C	Literature M. P., °C
16	 **7p**	80[e]	195–197	191–193[40]
17	 **7q**	92[c]	161–163	160–162[39]
18	 **7r**	65[d]	107–110	110–112[39]
19	 **7s**	67[d]	103–104	101–102[35]
20	 **7t**	73[c]	132–134	130–132[40]
21	 **7u**	72[e]	146–148	144–147[40]
22	 **7v**	78[c]	254–256	New compound

[a]Isolated yield after purification; [b]product was purified by recrystallization in ethanol; [c]product was purified by column chromatography mobile phase hexane: ethyl acetate; [d]product was purified by recrystallization in chloroform; [e]product was purified by column chromatography mobile phase chloroform

Further, the scope of the reaction has extended with the aliphatic aldehydes like crotonaldehyde, propionaldehyde, acetaldehyde and formaldehyde with *o*-phenylenediamine and *o*-aminothiophenol. The reaction has not proceeded with aliphatic aldehydes and has not afforded the desired product.

Although the exact mechanism is not clear, a proposed mechanism for the formation of benzimidazole and benzothiazole is shown in Scheme 5. In first step the aldehyde (**A**) oxygen was protonated by abstraction of proton from DBUHI3 complex to form compound (**C**) and liberate DBUI3 complex. Simultaneously liberated DBUI3 complex, I^- abstract the hydrogen from amines (**B**) to form compound (**D**) and liberates DBUI2 complex. In next step, **C** and **D** reacted to form intermediate (**E**). The intermediate **E** on reaction DBUI2 complex, DBU

abstract the proton of XH to form X^- and iodine coordinate with I_2 undergo cyclization to form intermediate **G** which undergo oxidative elimination to form C=N double bond to formed final product (**H**).



Scheme 5. Tentative mechanism of DBU-H–I_3 catalyzed synthesis of benzimidazole and benzothiazole.

CONCLUSION

In the present work, we have prepared the new R3NHI3 complexes and studied their catalytic activity in the preparation of 2-aryl substituted benzimidazole and benzothiazole derivatives. Among the screened amine–iodine catalysis, DBUHI3 was found an efficient catalyst for the preparation of 2-aryl substituted benzimidazole and benzothiazole. We believe that the present method is more convenient, efficient, greener, simpler and environmentally benign compared to most reported methods in the literature. The present method has not afforded the benzimidazole and benzothiazole derivatives with aliphatic aldehydes.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/11893, or from the corresponding author on request.

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ИЗВОД

КОМПЛЕКС DBUHI3 КАО ЕФИКАСАН КАТАЛИЗАТОР ЗА СИНТЕЗУ ДЕРИВАТА 2-ФЕНИЛБЕНЗИМИДАЗОЛА И БЕНЗОТИАЗОЛА

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У овом раду је описана једноставна синтеза различитих бензимидазола/бензотиазола, употребом DBU–јод–јодида као једноставног и еколошки прихватљивог катализатора. Настаје комплекс R3NHI3 у реакцији смеше амонијум-јодида, молекулског јода и амонијака у води. Структура комплекса R3NHI3 потврђена је спектроскопским техникама. Каталитичка својства добијеног амин–јодидног комплекса су испитане у реакцији синтезе бензимидазола/бензотиазола. Од испитаних катализатора DBUHI3 комплекс се показао као ефикасан. Синтеза бензимидазола и бензотиазола је постигнута у реакцијама *o*-фенилендиамина/*o*-аминотиофенола са различитим супституисаним арил-алдехидима користећи DBUHI3 комплекс као катализатор. У односу на друге, приказани протокол има неколико предности, као што су благи реакциони услови, комерцијално доступни прекурсори, катализатор који није скуп, кратко реакционо време, ширк опсег супстрата, висок принос, једноставан поступак изоловања производа, и поступак који није штетан за животну средину.

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