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EDITORIAL

Boric acid-catalyzed multi-component reaction for efficient synthesis of 4*H*-isoxazol-5-ones in aqueous medium

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Abstract The one-pot three-component reaction of aryl aldehydes with hydroxylamine hydrochloride and ethyl 3-oxobutanoate/ethyl 4-chloro-3-oxobutanoate/ethyl 3-oxo-3-phenylpropanoate in the presence of boric acid, H_3BO_3, in water leads to 4*H*-isoxazol-5(4*H*)-ones in high yields. The merits of this method are efficiency, simplicity, clean, green, easy work-up, high yields, and shorter reaction times.

Keywords Isoxazol · Three-component reaction · Boric acid · Green

Introduction

Multi-component reactions (MCRs) have been proven to be a very powerful method for the synthesis of highly functionalized molecules in a single reaction vessel. These reactions have a particular importance in the synthesis of biologically active compounds and natural products due to their significant features such as high efficiency, minimization of waste, versatility, facial completing, atom economy, and excellent functional group compatibility. Also, MCRs in water can be visualized as a well-designed synthetic method to attain a wide range of diverse molecular frameworks [1–3].

On the other hand, the synthesis of small heterocyclic systems containing an isoxazol ring occupies a significant place in pharmaceutical chemistry and organic synthesis. One of the best methods for achieving these systems is the use of MCRs. This five-membered heterocyclic unit represents a class of heterocyclic compounds with biological activities and medicinally useful agents such as anticonvulsant [4], antifungal [5], analgesic [6], antitumor [7], antioxidant [8], antimicrobial [9],

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COX-2 inhibitory [10], anti-inflammatory [11], antiviral [12], and antimycobacterial [13], as well as being used for the treatment of leishmaniasis [14] and of patients with active arthritis [15]. Furthermore, the isoxzolon core can also be used as the basis for the design and construction of merocyanine dyes, which are used in optical recording and nonlinear optical research [16].

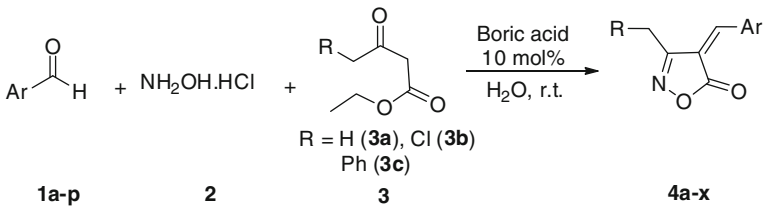
Boric acid, H_3BO_3, is a white solid moderately soluble in water, and is considered a very weak acid, with a presented ionization constant of about pKa = 9.2 [17]. It is a very stable compound and relatively benign to humans [18].

The development of mild, low-cost and high-performance acid catalysts has attracted much interest for green chemistry [19]. Recently, the organic synthesis of boric acid has attracted great interest because it is commercially available, environmentally benign, inexpensive, and easy to handle. Recently, this reagent has been used in various reactions including aza-Michael reaction [20], transesterification of ethyl acetoacetate [21], oxidation of sulfides [22], Biginelli reaction [23], and Mannich reaction [24]. In addition, it has also been used for the preparation of compounds such as the synthesis of 1,5-benzodiazepine derivatives [25], 2-amino-3,5-dicarbonitrile-6-thio-pyridines [26], 1-amidoalkyl-2-naphthols [27], dibenzoxanthenes [28], α-aminophosphonates [29], β-acetamido ketones [30], and α-hydroxyamides [31].

As recently reported, arylmethylene isoxazol-5(4*H*)-ones were prepared by using sodium benzoate [32], sodium sulfide [33], and sodium silicate [34] as the catalyst. Also, we synthesized the same arylmethylene isoxazol-5(4*H*)-ones by using of sodium ascorbate as the catalyst [35]. With this methodology as background, we attempted to develop an alternative catalyst for the preparation of arylmethylene isoxazol-5(4*H*)-ones. Although 4*H*-isoxazol-5-ones have so far been synthesized [31–38], to the best of our knowledge, no reports that include the use of boric acid for condensation of aromatic aldehydes (**1**), β-ketoesters (**3**), and hydroxylamine hydrochloride (**2**) have been reported. We here report the preparation of 4*H*-isoxazol-5-ones (**4a**-**x)** by one-pot three-component condensation of aryl aldehydes (**1**), hydroxylamine hydrochloride (**2**), and ethyl 3-oxobutanoate (**3a**)/ethyl 4-chloro-3-oxobutanoate (**3b**)/ethyl 3-oxo-3-phenylpropanoate (**3c**) using boric acid, H_3BO_3, as a green and reusable catalyst in water at room temperature (Scheme 1).

Experimental

All the reagents and chemicals were obtained from commercial sources and used without further purification. Melting points were measured on a Buchi 510 melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu FT-IR 8300 Spectrophotometer using the KBr pellets technique. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a BRUKER AVANCE DRX-400 MHz spectrophotometer using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as an internal standard. The purity of newly synthesized compounds and the development of reactions were monitored by thin layer chromatography (TLC) on Merck pre-coated silica gel 60 F_{254} aluminum sheets, visualized by UV light.



Scheme 1 One-pot three-component condensation of aryl aldehydes (**1a–p**), hydroxylamine hydrochloride (**2**), and β-ketoesters (**3a**, **b**, **c**) using boric acid

General procedure for preparation of 4*H*-isoxazole-5(4*H*)-ones (**4a-x**)

A mixture of equimolar quantities of hydroxylamine hydrochloride **2** (0.07 g, 1 mmol) and β-ketoester **3** (0.130 g, 1 mmol) were stirred in 5 mL of water for 5 min. Then, aryl aldehyde **1a–p** (1 mmol) and 10 mol % of boric acid was added and the reaction mixture was stirred at room temperature for the indicated time shown in Table 2 (below). The solid product formed was isolated by simple filtration and washed with water (5 mL). The products obtained were shown to be pure by TLC and spectral techniques. The filtrate was evaporated to remove water, leaving the catalyst. The same catalyst was employed to synthesize further derivatives. If necessary, further purification was performed by recrystallization from suitable solvents such as EtOH to give the desired compounds in high yields. The products are known and their identity was confirmed by comparison of their physical and spectroscopic data with those available in recent papers [31–38].

Selected spectral data

4-benzylidene-3-methylisoxazol-5(4*H*)-one (**4a**): ^{1}H NMR (400 MHz, CDC1$_3$): δ 2.34 (s, 3H), 7.46 (s, 1H), 7.55 (t, $J = 7.8$ Hz, 2H), 7.61–7.64 (m, 1H), 8.38 (dd, $J = 1.3$, 7.4 Hz, 2H).

3-methyl-4-(4-methylbenzylidene)isoxazol-5(4*H*)-one (**4c**): ^{1}H NMR (400 MHz, CDC1$_3$): δ 2.33 (s, 3H), 2.48 (s, 3H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.42 (s, 1H), 8.32 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDC1$_3$): δ 11.6, 22.1, 118.2, 129.8, 129.9, 134.2, 145.8, 150.2, 161.4, 168.3.

4-(3-hydroxybenzylidene)-3-methylisoxazol-5(4*H*)-one (**4f**): ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.28 (s, 3H), 7.08 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 7.6$ Hz, 1H), 7.85 (s, 1H), 7.95 (s, 1H), 9.96 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 11.7, 118.9, 119.9, 121.8, 125.8, 130.2, 134.1, 152.3, 157.8, 162.6, 168.2.

3-methyl-4-(thiophen-2-ylmethylene)isoxazol-5(4*H*)-one (**4 m**): ^{1}H NMR (400 MHz, CDC1$_3$): δ 2.32 (s, 3H), 7.29 (t, $J = 4.8$ Hz, 1H), 7.64 (s, 1H), 7.95 (d, $J = 4.8$ Hz, 1H), 8.13 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDC1$_3$): δ 11.5, 114.6, 128.9, 136.5, 139.2, 139.6, 141.5, 160.7, 168.7.

3-methyl-4-(thiophen-3-ylmethylene)isoxazol-5(4*H*)-one (**4n**): ^{1}H NMR (400 MHz, CDC1$_3$): δ 2.29 (s, 3H), 7.42 (dd, $J = 5.2$, 2.8 Hz, 1H), 7.49 (s, 1H),

7.95 (dd, $J = 4.8$, 1.6 Hz, 1H), 8.99 (dd, $J = 2.8$, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDC1_3$): δ 11.6, 117.0, 126.8, 131.5, 135.2, 139.4, 140.9, 161.3, 168.5.

3-(chloromethyl)-4-(4-hydroxybenzylidene)isoxazol-5(4*H*)-one (**4v**): ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.90 (s, 2H), 7.10 (d, $J = 8.4$ Hz, 2H), 8.04 (s, 1H), 8.48 (d, $J = 8.8$ Hz, 2H), 11.28 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 35.6, 110.7, 116.9, 124.9, 138.6, 153.3, 162.2, 164.9, 168.9.

3-(chloromethyl)-4-(4-(dimethylamino)benzylidene)isoxazol-5(4*H*)-one (**4w**): ^{1}H NMR (400 MHz, $CDC1_3$): δ 3.22 (s, 6H), 4.56 (s, 2H), 6.78 (d, $J = 8.6$ Hz, 2H), 7.55 (s, 1H), 8.48 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDC1_3$): δ 35.7, 40.3, 107.3, 111.7, 121.7, 138.3, 150.4, 154.8, 160.6, 169.9.

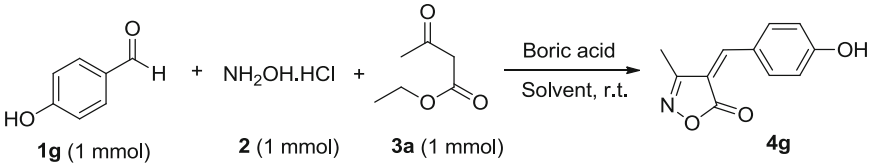
3-(chloromethyl)-4-(thiophen-2-ylmethylene)isoxazol-5(4*H*)-one (**4x**): ^{1}H NMR (400 MHz, $CDC1_3$): δ 4.60 (s, 2H), 7.34–7.36 (m, 1H), 7.98 (s, 1H), 8.06 (d, $J = 4.8$ Hz, 1H), 8.19 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDC1_3$): δ 35.3, 111.1, 129.2, 136.5, 140.9, 141.0, 142.6, 159.7, 168.3.

Results and discussion

The synthesis of arylmethylidene-isoxazole-5(4*H*)-ones is outlined in Scheme 1. In the beginning, equimolar quantities of benzaldehyde (**1a**), hydroxylamine hydrochloride (**2**), and ethyl acetoacetate (**3a**) were treated at room temperature in the presence of catalytic amounts of boric acid in water. In this reaction, compound **4a** was achieved in high yield. Compound **4a** has been described in the literature [31–34]. The structure of the compound **4a** was established from the spectral and physical data. The ^{1}H NMR spectrum of **4a** displayed two singlet peaks at $\delta = 2.34$ for the methyl group and $\delta = 7.46$ ppm for the olfinic proton of the C=C double bond. Aromatic protons of **4a** resonate as a triplet at $\delta = 7.55$, a doublet of doublets at $\delta = 8.38$ and multiplets in the region of $\delta = 7.61$–7.64 ppm. Also, the melting point of the compound **4a** was recorded and fixed with authentic samples showing that **4a** has been formed.

With the intention of investigating the optimum amounts of catalyst, the reaction of 4-hydroxybenzaldehyde (**1 g**) hydroxylamine hydrochloride (**2**), and ethyl acetoacetate (**3a**) as the model was conducted in water with different amounts of boric acid ranging from 5 to 20 mol % at room temperature (Table 1). As shown in Table 1, when the amount of boric acid was increased from 5 to 10 mol %, the yield of **4 g** was improved from 83 to 93 % (Table 1, entries 1–2). However, when the amount of boric acid was further raised to 20 mol %, remarkable increases in the yield of **4 g** were not observed (Table 1, entries 3–4). Consequently, the amount of 10 mol % boric acid was selected as the catalyst for these reactions. In addition, to search for the optimal solvent, the synthesis of **4 g** was accomplished by using solvents of water, acetone, 1,4-dioxane, ethanol, hexane, and a mixture of water–ethanol (V:V, 1:1) at room temperature (Table 1, entries 5–9). As can be seen in Table 1, the reaction in water led to higher yields and shorter reaction times than the others. As a consequence, water was nominated as the suitable solvent. Therefore, all further reactions were carried out using 10 mol % of boric acid in water at room temperature.

Table 1 Synthesis of **4g** in the presence of different solvents and amounts of catalyst[a]



1g (1 mmol) **2** (1 mmol) **3a** (1 mmol) **4g**

Entry	Solvent	Amounts of catalyst (mol %)	Time (min)	Yield (%)[b]
1	H_2O	5	100	83
2	H_2O	10	100	93
3	H_2O	15	100	90
4	H_2O	20	100	91
5	EtOH	10	100	75
6	1,4-Dioxane	10	150	35
7	Hexane	10	150	45
8	Acetone	10	120	40
9	H_2O:EtOH (1:1)	10	100	88
10	Solvent free	10	100	25

[a] Reaction conditions: 4-hydroxybenzaldehyde **1 g** (1 mmol), hydroxylamine hydrochloride **2** (1 mmol), ethyl acetoacetate **3** (1 mmol), water (5 mL), room temperature

[b] Isolated yield of product

With the optimized reaction conditions in hand, the expediency of this method was well evaluated using a variety of aryl aldehydes and β-ketoesters, and a series of compounds **4** were synthesized with this simple approach. The results are summarized in Table 2. The nature and position of the functional groups on the phenyl ring affected the yields of the products and the reaction times. The results indicated that aromatic aldehydes bearing electron-donating groups, such as $–OCH_3$, $–CH_3$, –OH, and $–N(Me)_2–$, are suitable for this reaction and the corresponding products were prepared in high yields (Table 2, entries 2–8, 18–23). However, the 2-hydroxybenzaldehyde yielded the corresponding isoxazol-5(4*H*)-one derivative in relatively lower yield, presumably due to its higher crowded steric (Table 2, entry 5). On the other hand, aryl aldehydes containing electron-withdrawing functional groups, such as –Cl or $–NO_2$, were ineffective and did not proceed under the optimized reaction conditions. Therefore, they are not suitable for this reaction (Table 2, entries 9–11). The current reaction was further examined using electron-rich heterocyclic aryl aldehydes such as furan-2-carbaldehyde, thiophene-2-carbaldehyde, and thiophene-3-carbaldehyde (Table 2, entries 12–14, 24). In this case, the reaction proceeded well with high yields. Interestingly, when 4-hydroxy-3-nitrobenzaldehyde was used, compound **4p** was obtained in high yield and shorter reaction time (Table 2, entry 16).

The structures of the title products were deduced from their spectra analysis. For instance, the ^{1}H NMR spectrum of 3-(chloromethyl)-4-(thiophen-2-ylmethylene)-

Table 2 Synthesis of 4*H*-isoazol-5(4*H*)-ones (**4**)[a]

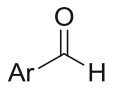
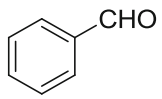
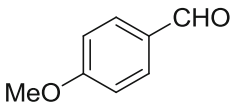
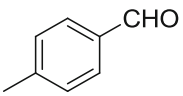
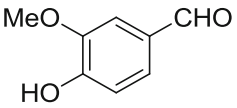
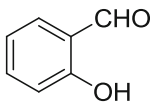
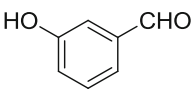
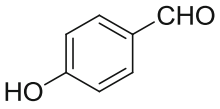
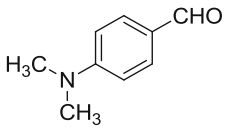
Entry		R	Product	Time (min)	Yield (%)[b]	Mp (°C)	
						Found	Reported[c]
1	 **1a**	H	**4a**	100	90	140–142	141–143
2	 **1b**	H	**4b**	50	92	174–175	174–176
3	 **1c**	H	**4c**	75	90	136–137	135–136
4	 **1d**	H	**4d**	85	95	214–215	211–214
5	 **1e**	H	**4e**	140	82	198–199	198–201
6	 **1f**	H	**4f**	100	94	201–203	202–203
7	 **1g**	H	**4 g**	100	93	214–215	214–216
8	 **1h**	H	**4 h**	90	93	226–228	227–228

Table 2 continued

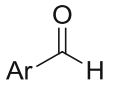
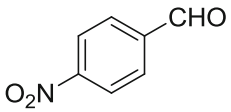
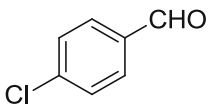
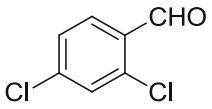
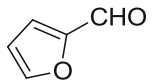
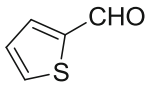
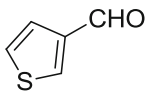
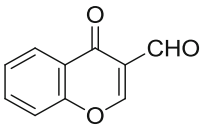
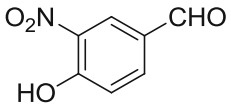
Entry		R	Product	Time (min)	Yield (%)[b]	Mp (°C)	
						Found	Reported[c]
9	 **1i**	H	**4i**	900	Trace	–	–
10	 **1j**	H	**4j**	900	Trace	–	–
11	 **1k**	H	**4 k**	1,440	Trace	–	–
12	 **1l**	H	**4 l**	90	89	239–241	238–241
13	 **1m**	H	**4 m**	75	91	146–147	146–147
14	 **1n**	H	**4n**	80	90	145–147	146–147
15	 **1o**	H	**4o**	120	90	242–244	241
16	 **1p**	H	**4p**	50	86	266–267	267–268

Table 2 continued

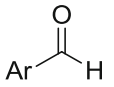
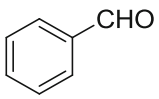
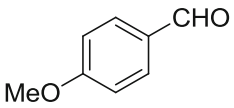
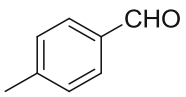
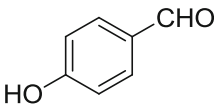
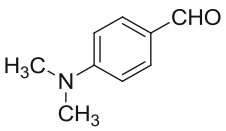
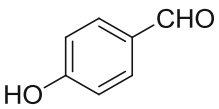
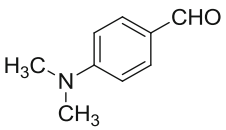
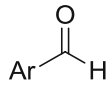
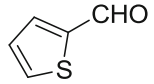
Entry		R	Product	Time (min)	Yield (%)[b]	Mp (°C)	
						Found	Reported[c]
17	 **1a**	Ph	**4q**	100	85	213–215	215–216
18	 **1b**	Ph	**4r**	70	91	168–170	168–169
19	 **1c**	Ph	**4 s**	75	90	195–196	194–196
20	 **1g**	Ph	**4t**	90	88	209–211	210
21	 **1h**	Ph	**4u**	95	92	195–197	194–196
22	 **1g**	Cl	**4v**	70	90	183–186	–
23	 **1h**	Cl	**4w**	80	92	179–180	–

Table 2 continued

Entry		R	Product	Time (min)	Yield (%)[b]	Mp (°C)	
						Found	Reported[c]
24	 **1m**	Cl	**4x**	70	89	146–148	–

[a] Reagents and conditions: aryl aldehyde **1** (1 mmol), hydroxylamine hydrochloride **2** (1 mmol), β-ketoester **3** (1 mmol), water (5 mL), room temperature

[b] All yields are of pure products after filtrated and recrystallization from ethanol

[c] Melting points are listed in refs. [32–39]

isoxazol-5(4*H*)-one (**4x**) revealed the structural characteristics of both thiophene and chloromethyl (Fig. 1). The ^{1}H NMR spectrum revealed distinctive singlet signals at $\delta = 4.60$ and 7.98 ppm for chloromethylene (—C$\underline{H_2}$Cl) and olfinic (>C=C$\underline{H}$—Ar) protons, respectively. Also, protons of the thiophene heterocyclic unit appear at $\delta = 8.06$ and 8.19 ppm, and in the region of $\delta = 7.34$–7.36 ppm. The

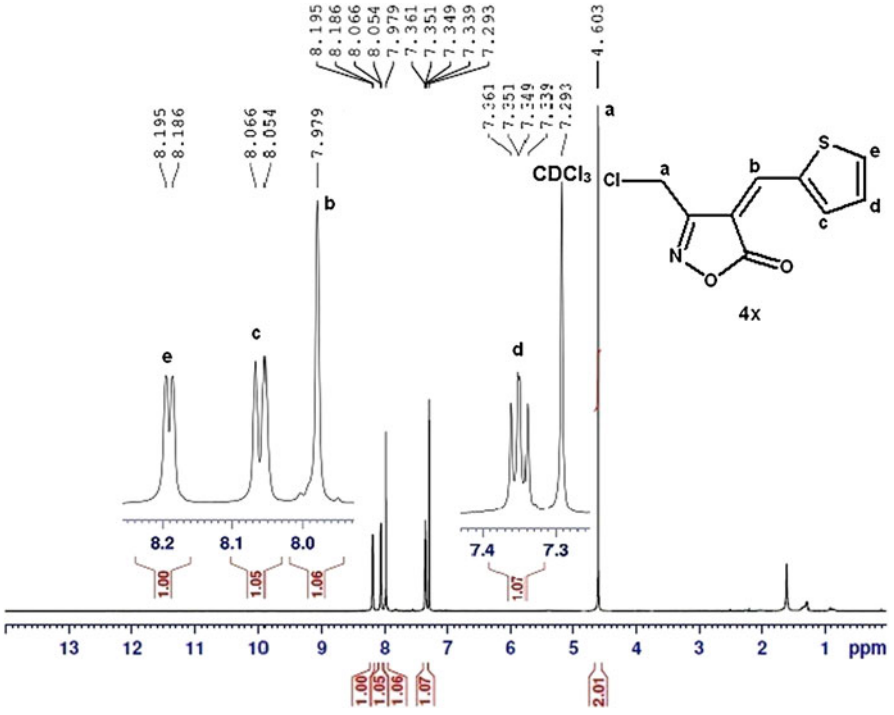
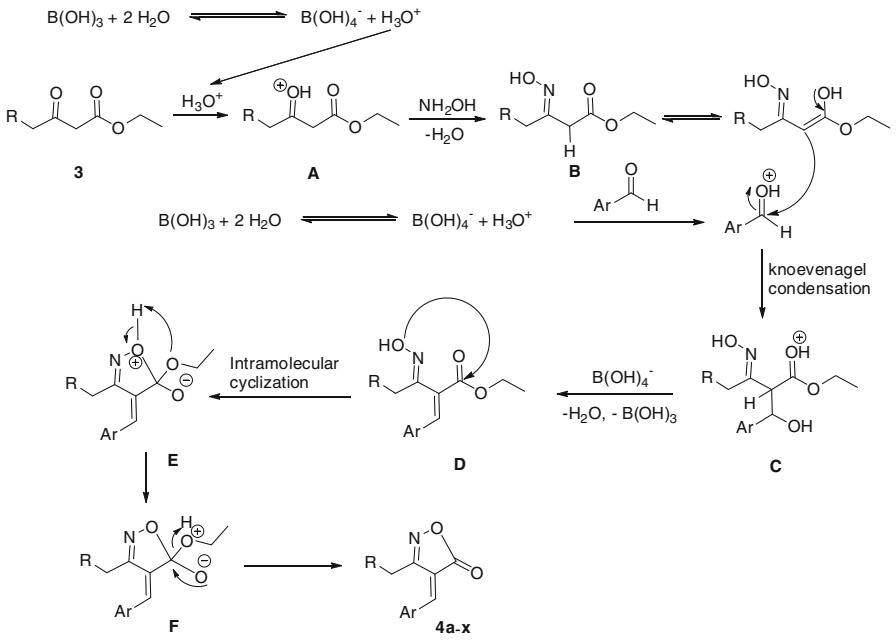


Fig. 1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(chloromethyl)-4-(thiophen-2-ylmethylene)isoxazol-5(4*H*)-one (**4x**)

^{13}C NMR spectrum of compound **4x** showed characteristic signals at $\delta = 35.3$ ppm for —$\underline{C}H_2Cl$, as well as 111.1, 159.7, and 168.3 ppm, for >$\underline{C}$=CH—Ar, C=N, and C=O of the isoxazol ring. The remaining five carbon resonances appearing between $\delta = 129.2$ and 142.6 ppm are due to the carbon atoms of the thiophene ring and C-b.

A plausible mechanism for the formation of the title compounds is shown in Scheme 2. To evaluate the proposed mechanism, we first tried to prepare the isoxazolon product with equivalent molar amounts of ethyl acetoacetate and hydroxylamine hydrochloride in water solvent in the presence of boric acid. The reaction was pursued by TLC. After completion of the reaction, the product was isolated, and then its infrared spectrum was recorded. The following peaks were observed on the IR-spectrum; 3,460, 1,695, and 1,600 cm^{-1}. The peak in the region of 3,460 cm^{-1} confirms the hydroxyl functional group in the intermediate. Also, the ester carbonyl group appeared in the region 1,695 cm^{-1} due to the hydrogen bond being shifted to lower frequencies. In isoxazolon intermediate products, the frequency of the carbonyl group should be shifted to a higher region, and the peak of OH eliminated. Accordingly, the isoxazolon product was not obtained. By adding an aromatic aldehyde to the mixture of ethyl acetoacetate and hydroxylamine hydrochloride, the final products (**4a**–**x**) were formed. This result probably reflects the formation of the oxime intermediate (**B**), and probably also represents the role of acid. Therefore, the formation of the title compounds proceeds via the Intramolecular cyclization intermediacy of a Knoevenagel adduct (**D**) of the preformed oxime of ethyl acetoacetate followed by ring closure in the presence of boric acid.



Scheme 2 Proposed mechanism for the formation of title compounds **4a-x**

Also, in our exploration of the reusability of the catalyst in water after completion of the reaction, the filtrate that remained as catalyst was subjected to evaporation under reduced pressure, and the recovery solid catalyst was applied as such for the consecutive runs in five series of the same model reaction under the optimized conditions for up to five runs (1st use: 90 %; isolated yield; 2nd use: 87 % isolated yield; 3rd use: 82 % isolated yield; 4th use: 76 % isolated yield; 5th use: 70 % isolated yield). Decreasing the yield is probably related to the slight reduction in the catalytic activity of the catalyst or the decreasin the the amount of catalyst recovery which is attributed to the handling.

Conclusion

In summary, the efficient and clean synthesis of 4-arylidene-3-methyl-isoxazol-5(4*H*)-ones (**4a**–**h** and **4l**–**p**), 4-arylidene-3-phenyl-isoxazol-5(4*H*)-ones (**4q**–**u**), as well as 3-(chloromethyl)-4-arylidene-isoxazol-5(4*H*)-ones (**4v**–**x**) via a one-pot three-component condensation of β-ketoesters (**3a**–**c**), aryl aldehydes, and hydroxylamine hydrochloride in the presence of boric acid as the catalyst at room temperature has been developed. The reaction exhibited such merits as mild conditions, easy work-up, completion of reaction in shorter reaction times, reuse of catalyst, safety, and use of water with its ecologically friendly point of view.

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