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Original article

DABCO-promoted facile and convenient synthesis of novel isoxazolyl-1*H*-2,3-pyrrole dicarboxylates

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ABSTRACT

Synthesis of isoxazolyl-1*H*-2,3-pyrrole dicarboxylate (**4**) was simply achieved by one-pot three component reaction of isoxazole amine (**1**) with diethyl acetylenedicarboxylate (DEAD) (**2**), and glyoxal (**3**), in acetonitrile catalyzed by diazabicyclo octane (DABCO).

1. Introduction

Pyrrole is one of the most important simple heterocycles, which is found in a broad range of natural products [1] and drug molecules, and is also of growing relevance in materials science [2]. Pyrrole derivatives have been given special emphasis due to a wide variety of medicinal and biological properties such as antitumor [3] and immunosuppresants [4] activity. They have also been recognized as versatile synthetic intermediates in organic synthesis [5]. These derivatives are used as organic conducting materials [6]. Biological activity of substituted isoxazoles has made them a focus of medicinal chemistry over the years. Isoxazole derivatives have been reported with diverse structural features and versatile biological properties such as antitumor [7], analgesic [8], antimicrobial [9], and for the treatment of hyper cholsteremia and hyperlipidemia [10], and as chemotherapeutic agents [11].

Synthesis of pyrrole derivatives has been achieved by the oxidative cyclization of β-enamino ketones and alkynoates using CuI in the presence of oxygen [12], coupling of phenyliodonium ylides and enamine esters using $BF_3{\cdot}Et_2O$ [13] silver catalyzed reaction between aldehydes and amines in a one pot condensation [14], intermolecular addition of oximes to activated alkynes and subsequent thermal rearrangement of *in situ* generated *O*-vinyl oximes [15], [4C+1N] cyclization of 4-acetylenic ketones with primary amines using $FeCl_3$ [16].

Although several protocols have been developed for the synthesis of pyrrole derivatives, many of these methods are associated with various drawbacks, such as harsh reaction conditions, tedious experimental procedures, unsatisfactory yields, and long reaction times. Hence, there is a need for a rapid and efficient method for the heterocyclic synthesis of pyrrole derivatives. As a part of our continuing effort toward the development of new methods [17], of expeditiously synthesizing bioactive compounds carrying isoxazole moiety, we here report a mild and efficient method for isoxazolyl-1*H*-2,3-pyrrole dicarboxylate scaffold using DABCO as a catalyst. This is a simple, rapid, one-pot and eco-friendly protocol for the synthesis of title compounds.

2. Experimental

All the melting points were determined on a Cintex melting point apparatus and are uncorrected. Analytical TLC was performed on Merck precoated 60 F_{254} silica gel plates. Visualization was done by exposing to iodine vapour. IR spectra (KBr pellet) were recorded on a PerkinElmer BX series FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker 75 MHz spectrometer. Chemical shift values are given in δ with tetramethyl silane as an internal standard. Mass spectral measurements were carried out by EI method on a JEOL JMC-300 spectrometer at 70 eV. Elemental analyses were performed on a Carlo Erba 106 and Perkin-Elmer model 240 analyzers.

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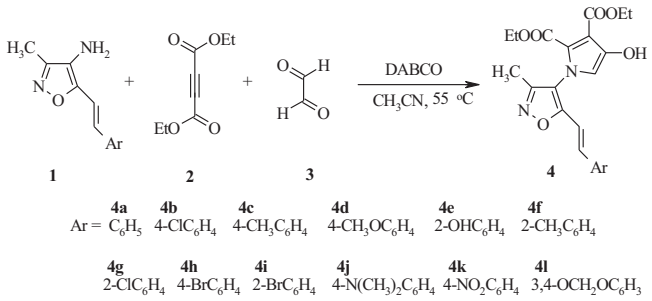
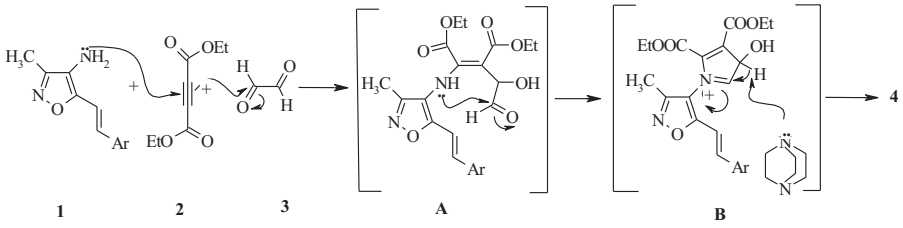


Scheme 1. One-Pot synthesis of isoxazolyl pyrroles.



Scheme 2. Plausible mechanism for pyrrole ring formation.

Synthesis of diethyl-4-hydroxy-1-3-methyl-5-[(E)-2-aryl-1-ethenyl]-4-isoxazolyl-1H-2,3-pyrrole dicarboxylate **4***:* To a stirred solution of 4-amino-3-methyl-5-styrylisoxazole (**1**) (1 mmol), in CH_3CN (15 mL) DABCO 10 mol% were added. The reaction mixture was refluxed with stirring at 55 °C for 30 min to this diethyl acetylenedicarboxylate (DEAD) (**2**) (1 mmol), glyoxal (**3**) (1 mmol) was added, and the reaction continued for another 4 h at 55 °C. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure, and 30 mL water was added to the residue, which was then extracted with ethyl acetate and the residue was purified by recrystallization in methanol to produce **4** in high yield (Scheme 1).

3. Results and discussion

4-Amino-3-methyl-5-styrylisoxazoles **1**, required for synthesis of target compounds was obtained by Knoevenagel condensation of 3,5-dimethyl-4-nitroisoxazole with aromatic aldehydes in the presence of piperidine in ethanol [18] followed by reduction with $SnCl_2$–HCl [19]. The reaction of **1** with diethyl acetylenedicarboxylate **2** and glyoxal **3** in presence of DABCO in acetonitrile at 50 °C gave diethyl-4-hydroxy-1-3-methyl-5-[(*E*)-2-aryl-1-ethenyl]-4-isoxazolyl-1*H*-2,3-pyrrole dicarboxylate **4** by a one-pot three components reaction.

The generality of the reaction was investigated for the synthesis of various isoxazolyl pyrrole derivatives by reacting several substituted amino styrylisoxazoles having electron donating as well as electron attracting groups with glyoxal and DEAD in the presence of DABCO. In general, all the reactions were clean and isoxazolyl pyrrole derivatives were obtained in high yields. All the products were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectra [20].

The plausible mechanism for the synthesis of isoxazole substituted pyrroles in the presence of DABCO as catalyst involves is the nucleophilic addition of isoxazole amine with DEAD followed by the attack of the acetylenic bond with glyoxal **3** to give an intermediate **A**, which is not isolated. Amine attacks aldehyde group by intramolecular reaction in **A** to give **B**, which is not isolated. Proton abstraction by DABCO finally gives the title compound **4** (Scheme 2).

4. Conclusion

In conclusion, we have developed an efficient and facile method for the synthesis of isoxazolyl pyrrole derivatives by a one-pot three-component protocol involving isoxazole amine, DEAD and glyoxal using DABCO as a catalyst. This synthesis offers the benefit of a simple method of purification, which does require chromatography. The mild reaction conditions, operational simplicity, and high yields are the advantages of the protocol.

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[20] Analytical data for compounds: **4a**: Pale brown; yield 90%, mp 143–145 °C; IR (KBr, cm^{-1}): ν 3446 (OH), 1740 (CO); ^1H NMR (300 MHz, $CDCl_3$): δ 1.59 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 2.28 (s, 3H, CH_3), 3.72 (q, 4H, *J* = 7.2 Hz, $2CH_2$), 6.68 (s, 1H, pyrrole–CH), 6.74 (d, 1H, *J* = 12 Hz, CH=CH), 6.91 (d, 1H, *J* = 12 Hz, CH=CH), 7.00–7.75 (m, 5H, ArH), 8.11 (s, 1H, OH, D_2O exchangeable). EI-MS [M]+ *m*/*z* 410. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.01, 16.32, 71.32, 101.62, 114.73, 116.34, 123.54, 123.78, 124.52, 127.38, 127.64, 128.20, 128.93, 129.47, 134.25, 136.41, 156.83, 159.72, 160.10, 168.45. Anal. Calcd. for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found C, 64.33; H, 5.42; N, 6.87. **4b**: Pale yellow; yield 93%, mp 161–163 °C; IR (KBr, cm^{-1}): ν 3432 (OH), 1738 (CO); ^1H NMR (300 MHz, $CDCl_3$): δ 1.61 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 2.26 (s, 3H, CH_3), 3.59 (q, 4H, *J* = 7.2 Hz, $2CH_2$), 6.51 (s, 1H, pyrrole–CH), 6.69 (d, 1H, *J* = 12 Hz, CH=CH), 6.90 (d, 1H, *J* = 12 Hz, CH=CH), 7.10–7.72 (m, 4H, ArH), 8.18 (s, 1H, OH, D_2O exchangeable). EI-MS [M]+ *m*/*z* 444. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.11, 16.28, 71.41, 101.58, 114.74, 116.31, 123.45, 123.81, 124.45, 127.30, 127.62, 128.55, 128.87, 129.41, 134.18, 136.42, 156.73, 159.70, 160.28, 168.45. Anal. Calcd. for $C_{22}H_{21}ClN_2O_6$: C, 59.40; H, 4.76; N, 6.30. Found C, 59.37; H, 4.80; N, 6.24. **4c**: Pale yellow; yield 88%, m.p. 153–155 °C; IR (KBr, cm^{-1}): ν 3442 (OH), 1745 (CO); ^1H NMR (300 MHz, $CDCl_3$): δ 1.70 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 2.30 (s, 3H, CH_3), 2.64 (s, 3H, $ArCH_3$), 3.48 (q, 4H, *J* = 7.2 Hz, $2CH_2$), 6.58 (s, 1H, pyrrole–CH), 6.67 (d, 1H, *J* = 12 Hz, CH=CH), 6.83 (d, 1H, *J* = 12 Hz, CH=CH), 6.98–7.66 (m, 4H, ArH), 8.15 (s, 1H, OH, D_2O exchangeable). EI-MS [M]+ *m*/*z* 424. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.16, 16.15, 28.43,71.38, 101.58, 114.70, 116.43, 123.56, 123.82, 124.57, 127.28, 127.64, 128.47, 128.88, 129.61, 134.14, 136.40, 156.69, 159.77, 160.28, 168.24. Anal. Calcd. for $C_{23}H_{24}N_2O_6$: C, 65.08; H, 5.70; N, 6.60. Found. C, 65.03; H, 5.73; N, 6.66. **4d**: Pale yellow; yield 90%, mp 148–150 °C; IR (KBr, cm^{-1}): ν 3440 (OH), 1742 (CO); ^1H NMR (300 MHz, $CDCl_3$): δ 1.66 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 2.26 (s, 3H, CH_3), 3.51 (q, 4H, *J* = 7.2 Hz, $2CH_2$), 3.62 (s, 3H, OCH_3), 6.61 (s, 1H, pyrrole–CH), 6.71 (d, 1H, *J* = 12 Hz, CH=CH), 6.87 (d, 1H, *J* = 12 Hz, CH=CH), 7.00–7.73 (m, 4H, ArH), 8.20 (s, 1H, OH, D_2O exchangeable). EI-MS [M]+ *m*/*z* 440. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.10, 16.19, 63.44,71.26, 101.45, 114.78, 116.45, 123.56, 123.71, 124.38, 127.42, 127.77, 128.59, 128.62, 129.79, 134.26, 136.57, 156.61, 159.75, 160.36, 168.39. Anal. Calcd. for $C_{23}H_{24}N_2O_7$: C, 62.72; H, 5.49; N, 6.36. Found C, 62.77; H, 5.44; N, 6.36. **4e**: Pale yellow; yield 87%, mp 160–162 °C; IR (KBr, cm^{-1}): ν 3443 (OH), 1746 (CO); ^1H NMR (300 MHz, $CDCl_3$): δ 1.63 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 2.30 (s, 3H, CH_3), 3.49 (q, 4H, *J* = 7.2 Hz, $2CH_2$), 6.60 (s, 1H, pyrrole–CH), 6.72 (d, 1H, *J* = 12 Hz, CH=CH), 6.86 (d, 1H, *J* = 12 Hz, CH=CH), 7.11–7.89 (m, 4H, ArH), 8.10 (s, 1H, OH, D_2O exchangeable), 8.22 (s, 1H, OH, D_2O exchangeable). EI-MS [M]+ *m*/*z* 426. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.19, 16.24, 71.39, 101.27, 114.55, 116.32, 123.45, 123.69, 124.40, 127.21, 127.53, 128.40, 128.73, 129.86, 134.41, 136.30, 156.44, 159.61, 160.29, 168.30. Anal. Calcd. for $C_{22}H_{22}N_2O_7$: C, 61.97; H, 5.20; N, 6.57. Found C, 61.93; H, 5.25; N, 6.52. **4f**: Pale yellow; yield 92%, mp 173–175 °C; IR (KBr, cm^{-1}): ν 3435 (OH), 1738 (CO); ^1H NMR (300 MHz, $CDCl_3$): δ 1.67 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 2.24 (s, 3H, CH_3), 2.60 (s, 3H, $ArCH_3$), 3.44 (q, 4H, *J* = 7.2 Hz, $2CH_2$), 6.51 (s, 1H, pyrrole–CH), 6.59 (d, 1H, *J* = 12 Hz, CH=CH), 6.70 (d, *J* = 12 Hz, 1H, CH=CH), 7.00–7.81 (m, 4H, ArH), 8.12 (s, 1H, OH, D_2O exchangeable). EI-MS [M]+ *m*/*z* 424. ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.98, 16.36, 27.42, 71.45, 101.42, 114.55, 116.52, 123.50, 123.77, 124.42, 127.38, 127.59, 128.41, 128.80, 129.63, 134.22, 136.51, 156.73, 159.81, 160.30, 168.11. Anal. Calcd. for $C_{23}H_{24}N_2O_6$: C, 65.08; H, 5.70; N, 6.60. Found C, 65.05; H, 5.68; N, 6.64. **4g**: Pale yellow; yield 90%, mp 157–159 °C; IR (KBr, cm^{-1}): ν 3432 (OH), 1738 (CO); ^1H NMR (300 MHz, $CDCl_3$): δ 1.68 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 2.22 (s, 3H, CH_3), 3.61 (q, 4H, *J* = 7.2 Hz, $2CH_2$), 6.59 (s, 1H, pyrrole–CH), 6.65 (d, 1H, *J* = 12 Hz, CH=CH), 6.72 (d, 1H, *J* = 12 Hz, CH=CH), 7.04–7.77 (m, 4H, ArH), 8.25 (s, 1H, OH, D_2O exchangeable). EI-MS [M]+ *m*/*z* 444. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.23, 16.18, 71.45, 101.41, 114.53, 116.28, 123.36, 123.78, 124.47, 127.41, 127.82, 128.41, 128.79, 129.32, 134.27, 136.50, 156.62, 159.75, 160.36, 168.26. Anal. Calcd. for $C_{22}H_{21}ClN_2O_6$: C, 59.40; H, 4.76; N, 6.30. Found C, 59.38; H, 4.79; N, 6.27. **4h**: Pale yellow; yield 92%, mp 154–156 °C; IR (KBr, cm^{-1}): ν 3425 (OH), 1745 (CO); ^1H NMR (300 MHz, $CDCl_3$): δ 1.68 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 2.30 (s, 3H, CH_3), 3.48 (q, 4H, *J* = 7.2 Hz, $2CH_2$), 6.55 (s, 1H, pyrrole–CH), 6.60 (d, 1H, *J* = 12 Hz, CH=CH), 6.71 (d, 1H, *J* = 12 Hz, CH=CH), 7.00–7.61 (m, 4H, ArH), 8.09 (s, 1H, OH, D_2O exchangeable). EI-MS [M]+ *m*/*z* 488. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.28, 16.41, 71.39, 101.47, 114.60, 116.28, 123.55, 123.68, 124.40, 127.37, 127.55, 128.42, 128.79, 129.29, 134.25, 136.36, 156.44, 159.51, 160.39, 168.51. Anal. Calcd. for $C_{22}H_{21}BrN_2O_6$: C, 54.00; H, 4.33; N, 5.73. Found C, 54.03; H, 4.30; N, 5.69. **4i**: Pale yellow; yield 91, mp 154–156 °C; Anal. Calcd. for $C_{22}H_{21}BrN_2O_6$: C, 54.00; H, 4.33; N, 5.73. Found C, 53.97; H, 4.38; N, 5.77. **4j**: Pale yellow; yield 91, mp 177–179 °C; Anal. Calcd. for $C_{24}H_{27}N_3O_6$: C, 63.56; H, 6.00; N, 9.27. Found C, 63.51; H, 6.04; N, 9.23. **4k**: Pale yellow; yield 93, mp 173–175 °C; Anal. Calcd. for $C_{22}H_{21}N_3O_8$: C, 58.02; H, 4.65; N, 9.23. Found C, 58.04; H, 4.63; N, 9.28. **4l**: Pale yellow; yield 89, mp 169–171 °C; Anal. Calcd. for $C_{23}H_{22}N_2O_8$: C, 60.79; H, 4.88; N, 6.16. Found C, 60.74; H, 4.93; N, 6.14.