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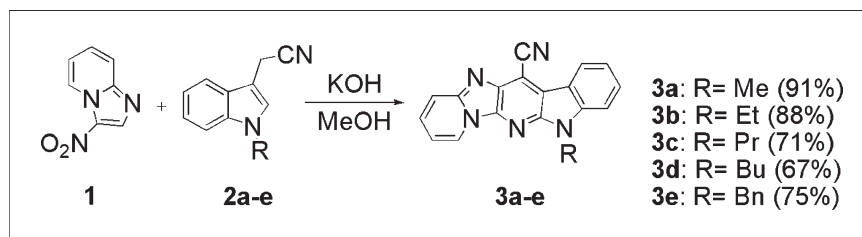
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Nucleophilic substitution of hydrogen in nitro derivative of imidazo[1,2-a]pyridine has been used as a key step in the one-pot synthesis of a new highly fluorescent heterocyclic system pyrido[1'',2'':1',2']imidazo[4',5':5,6]pyrido[2,3-b]indole.

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INTRODUCTION

It is well recognized and documented that addition of nucleophilic agents to electrophilic arenes proceeds faster in positions bearing hydrogen, resulting in the formation of the δ^{H} -adducts, rather than their addition in positions bearing leaving groups including halogens [1–3]. These δ^{H} -adducts can be further transformed into products of nucleophilic substitution of hydrogen *via* numerous mechanisms. One of the most general of these pathways is conversion of δ^{H} -adducts into nitroso compounds under proper conditions. This reaction can be considered as an intramolecular redox process with release of hydroxide ion. This conversion occurs usually in protic solvents apparently *via* protonation of the negatively charged oxygen of nitro group of the δ^{H} -adducts and elimination of water [4–7]. These nitrosoarenes are mostly cyclized to heterocyclic systems under the reaction conditions [8–12].

Continuing our study on the nucleophilic substitution reactions of hydrogen in imidazo[1,2-a]pyridine [13,14] and other heterocyclic systems [15–17], in this work, we have introduced a useful one-pot method for the synthesis of some fluorescent compounds through the conversion of imidazo[1,2-a]pyridine δ^{H} -adducts into nitroso compounds and transformation of them to a new heterocyclic system such as pyrido[1'',2'':1',2']imidazo[4',5':5,6]pyrido[2,3-b]indole-13-yl cyanides.

RESULTS AND DISCUSSION

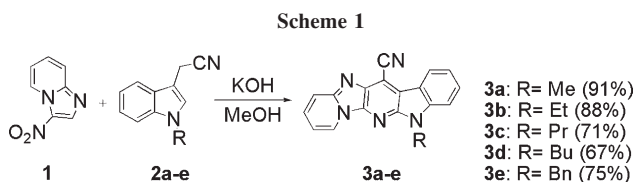
The new 5-alkyl-5H-pyrido[1'',2'':1',2']imidazo[4',5':5,6]pyrido[2,3-b]indole-13-yl cyanides **3a–e** were synthesized

via the nucleophilic substitution of hydrogen of imidazo[1,2-a]pyridine **1** with 2-(1-alkyl-1H-3-indolyl)acetonitrile **2a–e** in basic MeOH solution [4] in excellent yields (Scheme 1). A tentative mechanism to explain the formation of compounds **3a–e** is shown in Scheme 2.

The structural assignments of compounds **3a–e** were based on the analytical and spectral data. For example, in the ^1H NMR spectrum of **3a**, there are the signal at δ 4.03 ppm assignable to protons of methyl group and the doublet of doublet signal at δ 6.96 ppm ($J = 7.9$ Hz and $J' = 6.7$ Hz), the multiplet signals at δ 7.4–7.71 ppm, the doublet of signal at δ 8.58 (d, $J = 6.9$ Hz) and the doublet signal at δ 8.8 (d, $J = 8.4$ Hz) attributed to eight protons of aromatic rings. Moreover, the FTIR spectrum of **3a** in KBr showed the absorption band at 2240 cm^{-1} corresponding to cyanide group. All these evidences with the molecular ion peak at m/z 297 and microanalytical data strongly support the pentacyclic structure of compound **3a**.

These compounds are highly fluorescent. When a heteronitrogen is singly bonded to carbon atoms in a heterocycle, as in pyrrole rings (*e.g.*, indole, carbazole), the transitions involving the nonbonding electrons have properties similar to those of $\pi-\pi^*$ transitions. In fact, the nonbonding orbital is perpendicular to the plane of the ring, which allows it to overlap the p orbitals on the adjacent carbon atoms.

The fluorescence absorption and emission spectra of compounds **3a–e** were recorded at the concentration of 10^{-5} and 10^{-6} M in chloroform as the solvent. Figures 1 and 2 show the visible absorption and emission spectra of compounds **3a–e**. Values of molar extinction



coefficient (ϵ) were calculated as the slope of the plot of absorbance *versus* concentration. The fluorescence quantum yields (Φ_F) of compounds **3a–e** were determined *via* comparison methods, using fluorescence as a standard sample in 0.1 M NaOH and MeOH solution [14,18]. The λ_{max} , λ_{ex} , λ_{flu} , and fluorescence quantum yields (Φ_F) data are presented in Table 1.

In conclusion, we have presented a facile, efficient, and useful protocol for the synthesis of some fluorescent compounds from nitro derivative of imidazo[1,2-a]pyridine.

EXPERIMENTAL

Melting points were recorded on an Electrothermaltyp-9100 melting-point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrometer, and only noteworthy absorptions are listed. The ^{13}C NMR (125 MHz) and the ^1H NMR (500 MHz) spectra were recorded on a Bruker Avance DRX-500 Fourier transformer spectrometer. Chemical shifts are reported in ppm downfield from TMS as internal standard; coupling constant J are given in Hz. The mass spectra were recorded on a Varian Mat, CH-7 at 70 eV. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer. Absorption spectra were recorded on an Agilent 8453 spectrophotometer. Fluorescence spectra were recorded using Shimadzu RF-1501 spectrofluorophotometer. UV–vis and fluorescence scans were recorded from 350 to 700 nm. All measurements were carried out at room temperature. Compounds **1**

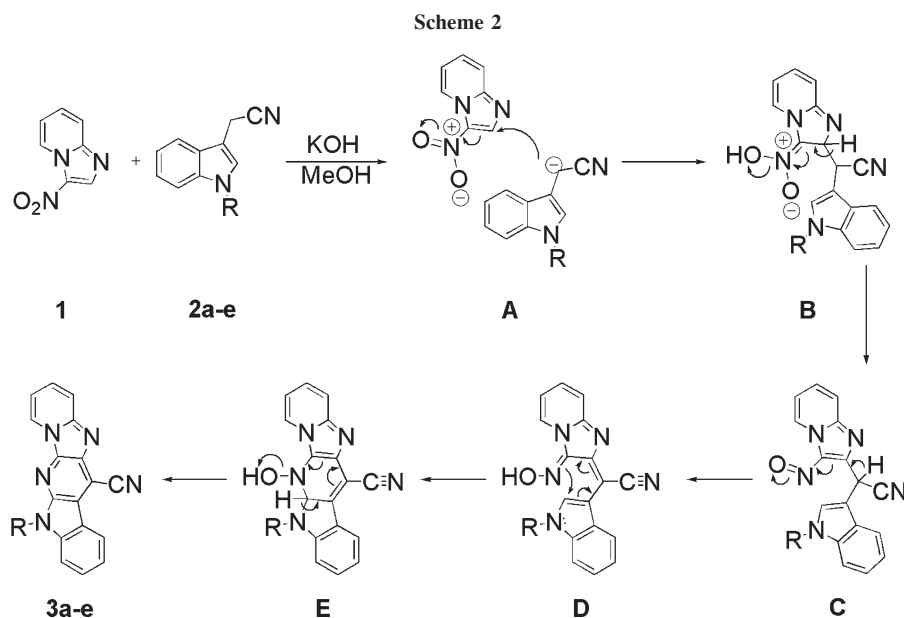
[19] and **2a–e** [20,21] were obtained according to the published methods. Other reagents were commercially available.

General procedure for the synthesis of 3a–e from 1 and 2a–e. Compounds **1** (1.63 g, 10 mmol) and **2a–e** (12 mmol) were added with stirring to a solution of KOH (20 g, 357 mmol) in methanol (80 mL). The mixture was refluxed with stirring for 2 h, and then poured into water, and then it was neutralized with dilute HCl solution. The precipitate was collected by filtration, washed with water, following with EtOH, and then air dried to give **3a–e**.

5-Methyl-5H-pyrido[1'',2'':1',2']imidazo[4',5':5,6]pyrido[2,3-b]indole-13-carbonitrile (3a). Compound **3a** was obtained as shining yellow needles (EtOH), yield (91%), mp 325–327°C; ^1H NMR (CDCl_3 , ppm): δ 4.03 (s, 3H, CH_3), 6.96 (dd, $J = 7.9$ Hz, $J' = 6.7$ Hz, 1H, pyridine), 7.4–7.71 (m, 5H, Phenyl and pyridine protons), 8.58 (d, $J = 6.9$ Hz, 1H, pyridine), 8.8 (d, $J = 8.4$ Hz, 1H, pyridine) ppm; ^{13}C NMR (CDCl_3 , ppm): δ 34.33, 101.11, 109.37, 111.23, 115.19, 116.9, 118.33, 118.87, 120.31, 122.59, 124.63, 128.58, 130.97, 132.08, 139.59, 140.62, 146.11, 148.45 ppm; IR (KBr disk): ν 2240 cm^{-1} (CN). MS (m/z) 297 (M^+). Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_4$ (297.3): C, 72.72; H, 3.73; N, 23.56. Found: C, 73.15; H, 3.82; N, 23.29.

5-Ethyl-5H-pyrido[1'',2'':1',2']imidazo[4',5':5,6]pyrido[2,3-b]indole-13-carbonitrile (3b). Compound **3b** was obtained as shiny yellow needles (EtOH), yield (88%), mp 288–289°C; ^1H NMR (CDCl_3 , ppm): δ 1.51 (t, $J = 7.2$ Hz, 3H, CH_3), 4.63 (q, $J = 7.2$ Hz, 2H, $-\text{CH}_2-$), 7.01 (dd, $J = 7.9$ Hz, $J' = 6.7$ Hz, 1H, pyridine), 7.27–7.81 (m, 5H, phenyl and pyridine protons), 8.61 (d, $J = 6.9$ Hz, 1H, pyridine), 8.83 (d, $J = 8.4$ Hz, 1H, pyridine) ppm; ^{13}C NMR (CDCl_3 , ppm): δ 13.93, 36.90, 100.22, 109.38, 111.27, 115.19, 116.94, 118.27, 118.74, 120.48, 122.61, 124.62, 128.58, 130.97, 132.07, 139.59, 140.62, 146.81, 148.43 ppm; IR (KBr disk): ν 2240 cm^{-1} (CN). MS (m/z) 311 (M^+). Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_4$ (311.3): C, 73.30; H, 4.21; N, 22.49. Found: C, 73.41; H, 4.20; N, 22.71.

5-Propyl-5H-pyrido[1'',2'':1',2']imidazo[4',5':5,6]pyrido[2,3-b]indole-13-carbonitrile (3c). Compound **3c** was obtained as shiny yellow needles (EtOH), yield (71%), mp 268–270°C; ^1H



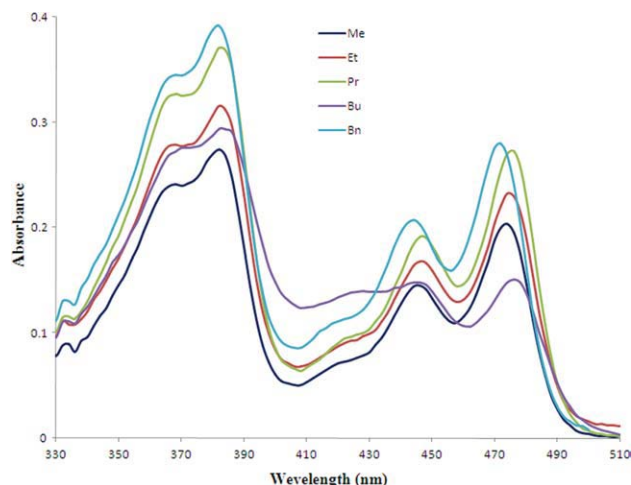


Figure 1. Visible absorption spectrum of compounds **3a–e** in dilute ($1 \times 10^{-5} M$) chloroform solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

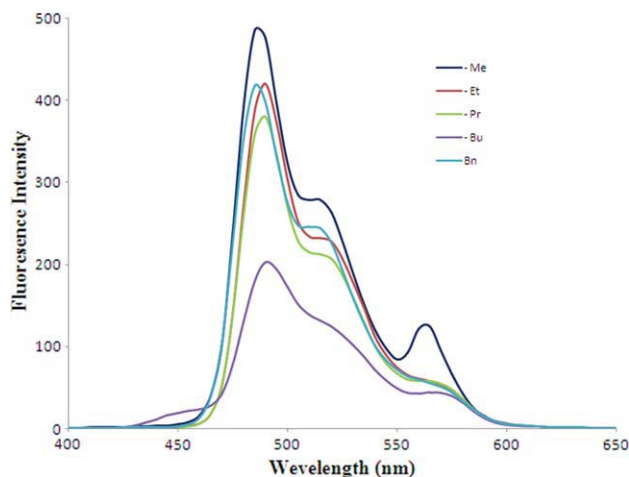


Figure 2. Emission spectrum of compounds **3a–e** in dilute ($1 \times 10^{-6} M$) chloroform solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1

Photophysical data for absorption (abs) and fluorescence (flu) of **3a–e**.

Dye	3a	3b	3c	3d	3e
λ_{\max} (nm) ^a	382, 446, 476	382, 446, 474	382, 446, 474	382, 446, 476	382, 444, 472
$\epsilon \times 10^{-4}$ ($M^{-1} \text{ cm}^{-1}$) ^b	2.74, 1.48, 2.03	3.15, 1.68, 2.32	3.71, 1.91, 2.72	2.94, 1.48, 1.51	3.92, 2.07, 2.80
λ_{ex} (nm) ^c	283	283	283	283	283
λ_{flu} (nm) ^d	485	490	490	490	485
Φ_{F} ^e	0.59	0.63	0.65	0.66	0.60

^a Wavelengths of maximum absorbance (λ_{\max}).

^b Molar extinction coefficient.

^c Wavelengths of fluorescence excitation (λ_{ex}).

^d Wavelengths of fluorescence emission (λ_{flu}).

^e Fluorescence quantum yield (Φ_{F}).

NMR (CDCl_3 , ppm): δ 1.02 (t, $J = 7.2$ Hz, 3H, CH_3), 1.81–2.16 (m, 2H, $-\text{CH}_2-$), 4.58 (t, $J = 7.2$ Hz, 2H, $-\text{CH}_2-$), 7.00 (dd, $J = 7.8$ Hz, $J' = 6.6$ Hz, 1H, pyridine), 7.38–7.88 (m, 5H, phenyl and pyridine protons), 8.68 (d, $J = 7.0$ Hz, 1H, pyridine), 8.9 (d, $J = 8.4$ Hz, 1H, pyridine) ppm; ^{13}C NMR (CDCl_3 , ppm): δ 10.55, 24.78, 39.38, 100.13, 109.38, 111.27, 115.19, 116.94, 118.27, 118.74, 120.48, 122.61, 124.62, 128.58, 130.97, 132.07, 139.59, 140.62, 146.95, 148.43 ppm; IR (KBr disk): ν 2240 cm^{-1} (CN). MS (m/z) 325 (M^+). Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_4$ (325.4): C, 73.83; H, 4.65; N, 21.52. Found: C, 73.41; H, 4.50; N, 21.71.

5-Butyl-5H-pyrido[1'',2'':1',2']imidazo[4',5':5,6]pyrido[2,3-b]indole-13-carbonitrile (3d). Compound **3d** was obtained as shiny yellow needles (EtOH), yield (67%), mp 232–235°C; ^1H NMR (CDCl_3 , ppm): δ 1.00 (t, $J = 6.7$ Hz, 3H, CH_3), 1.16–1.51 (m, 2H, $-\text{CH}_2-$), 1.75–2.01 (m, 2H, $-\text{CH}_2-$), 4.59 (t, $J = 6.7$ Hz, 2H, $-\text{CH}_2-$), 6.96 (dd, $J = 7.8$ Hz, $J' = 6.6$ Hz, 1H, pyridine), 7.26–7.90 (m, 5H, phenyl and pyridine protons), 8.58 (d, $J = 7.0$ Hz, 1H, pyridine), 8.8 (d, $J = 8.4$ Hz, 1H, pyridine) ppm; ^{13}C NMR (CDCl_3 , ppm): δ 13.94, 18.65, 33.45, 38.48, 100.08, 109.38, 111.27, 115.19, 116.94, 118.27, 118.74, 120.48, 122.61, 124.62, 128.58, 130.97, 132.07,

139.59, 140.62, 146.97, 148.43 ppm; IR (KBr disk): ν 2240 cm^{-1} (CN). MS (m/z) 339 (M^+). Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_4$ (339.4): C, 74.32; H, 5.05; N, 20.63. Found: C, 73.91; H, 5.15; N, 20.71.

5-Benzyl-5H-pyrido[1'',2'':1',2']imidazo[4',5':5,6]pyrido[2,3-b]indole-13-carbonitrile (3e). Compound **3e** was obtained as shiny yellow needles (EtOH), yield (75%), mp 276–278°C; ^1H NMR (CDCl_3 , ppm): δ 5.80 (s, 2H, $-\text{CH}_2-$), 7.05 (dd, $J = 7.9$ Hz, $J' = 6.7$ Hz, 1H, pyridine), 7.3–7.9 (m, 10H, phenyl and pyridine protons), 8.65 (d, $J = 6.9$ Hz, 1H, pyridine), 8.88 (d, $J = 8.4$ Hz, 1H, pyridine) ppm; ^{13}C NMR (CDCl_3 , ppm): δ 49.35, 101.07, 109.31, 111.40, 115.18, 116.87, 118.23, 118.69, 120.53, 122.62, 123.76, 124.61, 124.78, 125.03, 125.81, 128.59, 130.99, 132.07, 139.58, 140.62, 146.53, 148.43 ppm; IR (KBr disk): ν 2240 cm^{-1} (CN). Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_4$ (373.4): C, 77.20; H, 4.05; N, 18.75. Found: C, 77.41; H, 4.20; N, 18.51.

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