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An efficient solvent-free synthesis of imidazolines and benzimidazoles using $K_4[Fe(CN)_6]$ catalysis

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Abstract: Imidazolines and Benzimidazoles have been efficiently synthesized in high yields by treatment of 1,2-diamine with aldehydes using the metal co-ordinate complex $K_4[Fe(CN)_6]$ as a catalysis. The method was carried out under solvent free condition via oxidation of carbon-nitrogen bond. The process is green, mild and inexpensive.

Keywords: Aldehydes; $K_4[Fe(CN)_6]$; imidazolines; benzimidazoles; solvent free

1. Introduction

The development of simple, efficient and general synthetic method for biological active compounds from readily available catalyst is one of the major challenges in organic synthesis.

The importance of imidazolines and benzimidazloes units arises, because they are found in many biologically active compounds.[1-2] Imidazolines are biologically active pharmacophore and synthetic intermediates in medicinal chemistry.[3-5] They are also used as chiral catalysts,[6] chiral auxiliaries[7] and ligands for asymmetric catalysis.[8-9] As a continuation of our interest in the synthesis of imidazolines due to its broad spectrum of biological activities including antihyperglycemic,[10-11] antiinflammatory,[12-13] antihypertensive,[14-15] anticancer[16] and antihypercholesterolemic[17] agents. In addition, the benzimidazol moiety shown excellent biological activity like antiulcers, antihypertensives, antivirals, antifungals, anticancers, antihistaminics, antibacterial, antitubercular, antiasthmatic, anti-diabetic and antiprotozoal.[18-26]

Recently, several methods have been developed, for the synthesis of benzimidazoles in presence of various catalyst such as sulfur/ultrasonic,[27] homogeneous Lewis acids,[28] $I_2/KI/K_2CO_3/H_2O$,[29] pyridinium-p-toluenesulfonate,[30] ionic liquids,[31] polyaniline-sulfate,[32] (bromodimethyl)sulfonium bromide[33] and Zeolite. [34] However, all of the synthetic protocols reported so far suffer from disadvantages such as, use of organic solvents,[28,30,32] harsh reaction conditions,[29,33] excess temperature, [29] prolonged reaction times,[30,32] use of expensive reagents.[28,31] To overcome all this disadvantages we report a practical, inexpensive and green method for the synthesis of imidazolines and benzimidazoles by using potassium ferro-cyanide as a catalyst under solvent free condition.

In recent years, potassium ferro-cyanide has gained special attention as a catalyst in organic synthesis like synthesis of anti-Alzheimer drug(-) Galanthamine[35] due to its high stability, oxidizing power selectivity and a nontoxic by product Fe(III).It promoted oxidative cyclization of 5-S

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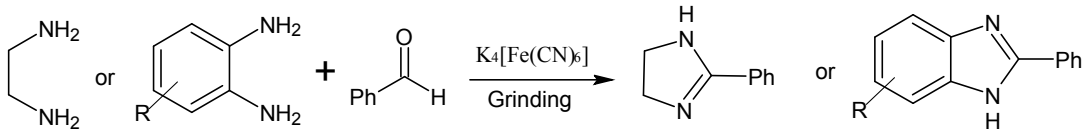
Cysteinyldopa [36]. Z. Y. Xiao et al studied the liberation of cyanide into the environment which has terristerial importance for ecosystem[37]. M. A. Gaffar et al studied the kinetic of the potassium ferro cyanide[38] because of many advantages such as excellent solubility in water, uncomplicated handling, inexpensiveness, eco-friendly nature, readily available and high reactivity.

2. Results and discussion

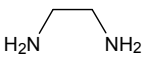
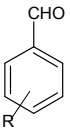
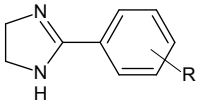
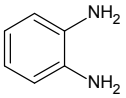
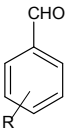
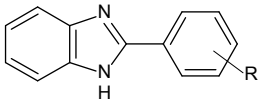
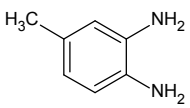
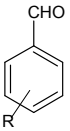
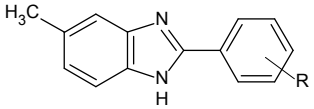
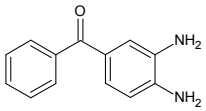
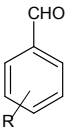
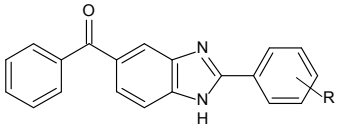
In this research article, we wish to report an efficient and practical method for the synthesis of imidazolines and benzimidazoles in excellent yields using cheaper and eco-friendly potassium ferro-cyanide catalyst. The reaction was carried out by grinding the mixture of 1,2-diamine (1.1 mmol), aldehyde (1 mmol) and catalytic amount of potassium ferro-cyanide (10 mol %) under solvent free condition to give the desired imidazolines and benzimidazoles in excellent yields (Scheme 1, Table 1).



Scheme 1. Synthesis of imidazolines and benzimidazoles

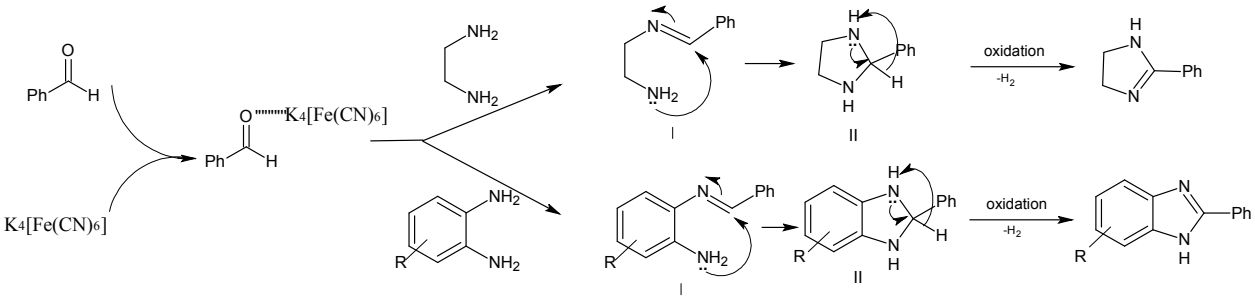
Accordingly, (10 mol%) of catalyst was sufficient to catalyze the reaction. However, no product formation was observed in absence of $K_4[Fe(CN)_6]$. By getting this result, we have extended this protocol to a variety of 1,2-diamines and aldehydes summarized in Table 1, aldehydes containing electron withdrawing substitution show fast reaction time, because it increases the electrophilic character of aromatic aldehyde towards the 1,2-diamine. In case of 1,2-diamines, 4-Methyl-o-phenylenediamine reacted fast because of electron donating nature of methyl group on aromatic ring, because it increases nucleophilic character of 1,2-diamine. In this protocol, all synthesized products obtained in excellent yield (90-97%).

Table 1. Synthesis of benzimidazoles and imidazolines

Entry	1,2-diamines	Aldehydes	Products (a-o)	Yield[a] (%)	mp (^{o}c) observed (lit.)
1			 R = **a.** 4-NO_2; **b.** 4-CH_3; **c.** 2,4-Cl; **d.** 4-$N(Me)_2$; **e.** 4-Br	**a.** 96 **b.** 94 **c.** 93 **d.** 94 **e.** 95	**a.** 228-231 (230-232[39]) **b.** 179-181 (177-179[39]) **c.** 107-108 (105-108[29]) **d.** 258-260 (258-260[29]) **e.** 243-245 (242-246[29])
2			 R = **f.** 4-CH_3; **g.** 4-OCH_3; **h.** H; **i.** 3-F,4-CF_3	**f.** 94 **g.** 92 **h.** 97 **i.** 90	**f.** 274-276 (275-276[41]) **g.** 222-225 (223-226[29]) **h.** 293-295 (295[22]) **i.** 165-167 (166[40])
3			 R = **j.** H; **k.** 4-NO_2; **l.** 3-F,4-CF_3	**j.** 95 **k.** 97 **l.** 96	**j.** 235-236 (335-336[40]) **k.** 240-242 (240-241[40]) **l.** 174-176 (174[31])
4			 R = **m.** H; **n.** 4-NO_2; **o.** 3-F,4-CF_3	**m.** 92 **n.** 94 **o.** 90	**m.** 219-221 (221-222[40]) **n.** 239-241 (240-241[40]) **o.** 225-227 (226-227[40])

[a] Isolated yield of the products

The possible mechanism of this reaction is shown in Scheme 2. The $K_4[Fe(CN)_6]$ increase the electrophilic character at aldehydic carbon, which will facilitate the nucleophilic addition of 1,2-diamines to gave an intermediate I, which on cyclisation followed by oxidation yields desired product.



Scheme 2. Proposed mechanism for the synthesis of imidazolines and benzimidazoles

3. Conclusion

In conclusion, we have first demonstrated that potassium ferro-cyanide can be used as a green catalyst for efficient synthesis of imidazolines and benzimidazoles under solvent free condition. A very simple, rapid, green, energy efficient and high yielding protocol makes this method a valid contribution to synthesize biological active imidazolines and benzimidazoles derivatives.

4. Experimental

All chemicals were purchased from Merck, Aldrich and Rankem Chemical Companies and used without further purification. Purity of the compounds were checked by thin layer chromatography (TLC) on Merck silica gel 60 F254 pre-coated sheets Melting points of the synthesized compounds were determined in open-glass capillaries on a stuart-SMP10 melting point apparatus. IR absorption spectra were recorded on a Perkin Elmer 1650 FTIR using KBr pellets in the range of 4000-450 cm^{-1}, ^{1}H-NMR spectra were recorded on a Bruker spectrometer operating at 200 MHz. The ^{1}H-NMR chemical shifts are reported as parts per million (ppm) downfield from TMS (tetramethylsilane) used as an internal standard. Mass spectra were recorded on LCQ ion trap mass spectrometer. All compounds were known, and obtained physical and spectroscopic data were compared with literatures data.

General procedure for the synthesis of imidazolines/ benzimidazoles

A mixture of substituted 1,2-diamine (1.1 mmol), aldehyde (1 mmol) and potassium ferro-cyanide (10 mol %) was crushed in a mortar with a pestle at room temperature. Progress of reaction was monitored by TLC. After completion of reaction (< 2 min) the crude product was washed with water, dried and recrystallized with ethyl acetate.

2-(4-Nitrophenyl)imidazoline (a): IR (KBr, cm^{-1}): ν 3187 (NH), 2940 (CH), 1681; ^{1}H NMR (DMSO-d_6, 200 MHz): d 8.03 (d, 2H, *J* = 8.1 Hz), 7.85 (d, 2H, *J* = 8.1 Hz), 4.37 (br, 1H), 3.58 (s, 4H); MS (ES) calcd for $C_9H_9N_3O_2$ (M^+) *m/z* 191.18, found 191.15.

2-(4-methylphenyl) imidazoline (b): R (KBr, cm^{-1}): ν 3143 (NH), 2933 (CH), 1620; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.38-6.95 (m, 4H), 4.27 (br, 1H), 3.47 (s, 4H), 2.38 (s, 3H); MS (ES) calcd for $C_{10}H_{12}N_2$ (M^+) *m/z* 160.21, found 160.17.

2-(2,4-Dichlorophenyl)imidazoline (c): IR (KBr, cm^{-1}): ν 3134 (NH), 2929 (CH), 1608; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.75–7.23 (m, 3H), 4.31 (br, 1H), 3.79 (s, 4H); MS (ES) calcd for $C_9H_8N_2Cl_2$ (M^+) *m/z* 215.08, found 215.11, 217.07 (MH^{+2})

2-(4-N,N-Dimethylaminophenyl)imidazoline (d):IR (KBr, cm^{-1}): ν 3177 (NH), 2960 and 2918 (CH), 1617; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.81 (d, 2H, *J* = 8.0 Hz), 6.89 (d, 2H, *J* = 8.0 Hz), 4.77 (s, 4H), 4.38 (br, 1H), 3.04 (s, 6H); MS (ES) calcd for $C_{11}H_{15}N_3$ (M^+) *m/z* 189.26, found 189.21.

2-(4-Bromophenyl)imidazoline (e): IR (KBr, cm^{-1}): ν 3187 (NH), 2961 and 2941 (CH), 1608; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.81–7.70 (m, 4H), 4.31 (br, 1H), 3.85 (s, 4H); MS (ES) calcd for $C_9H_9N_2Br$ (M^+) *m/z* 225.08, found 225.03

2-(4-methylphenyl)-1*H*-benzimidazole (f): IR (KBr, cm^{-1}): ν 3147 (NH), 2948 (CH), 1665; ^{1}H NMR ($CDCl_3$/DMSO-d_6, 200 MHz): δ 7.60 (m, 2H), 7.23 (dd, 2H, *J* = 8.1, 1.2 Hz), 7.17 (m, 2H), 6.97 (dd, 2H, *J* = 8.1, 1.2 Hz), 3.97 (brs, 1H), 2.37 (s, 3H); MS (ES) calcd for $C_{14}H_{12}N_2$ (M^+) *m/z* 208.25, found 208.21.

2-(4-methoxyphenyl)-1*H*-benzimidazole (g): IR (KBr, cm^{-1}): ν 3151 (NH), 2949 (CH), 1621; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.60 (m, 2H), 7.17 (dd, 2H, *J* = 7.8, 1.2 Hz), 7.09 (m, 2H), 6.75 (dd, 2H, *J* = 7.8, 1.2 Hz), 4.15 (brs, 1H), 3.57 (s, 3H); MS (ES) calcd for $C_{14}H_{12}N_2O$ (M^+) *m/z* 224.25, found 224.21.

2-phenyl-1*H*-benzimidazole (h): IR (KBr, cm^{-1}): ν 3172 (NH), 2937 (CH), 1637; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.63 (m, 2H), 7.35-7.16 (m, 7H), 4.23 (brs, 1H); MS (ES) calcd for $C_{13}H_{10}N_2$ (M^+) *m/z* 294.23, found 294.17.

2-[3-fluoro-4-(trifluoromethyl)phenyl]-1*H*-benzimidazole (i):IR (KBr, cm^{-1}): ν 3187 (NH), 2945 (CH), 1632;^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.67-7.16 (m, 7H), 4.07 (brs, 1H); MS (ES) calcd for $C_{14}H_8F_4N_2$ (M^+) *m/z* 280.22, found 280.19.

5-methyl-2-phenyl-1*H*-benzimidazole (j): IR (KBr, cm^{-1}): ν 3181 (NH), 2935 (CH), 1610;^{1}H NMR (200 MHz, $CDCl_3$): δ 7.47-7.39 (m, 4H), 7.21-7.17 (m, 3H), 6.95-6.89 (m, 1H), 3.51 (brs, 1H), 2.18 (s, 3H),; MS (ES) calcd for $C_{14}H_{12}N_2$ (M^+) *m/z* 208.25, found 208.15.

5-methyl-2-(4-nitrophenyl)-1*H*-benzimidazole (k): IR (KBr, cm^{-1}): ν 3241 (NH), 2949 (CH), 1647;^{1}H NMR ($CDCl_3$/DMSO-d_6, 200 MHz): δ 8.14 (dd, 2H, J = 8.1, 2.0 Hz), 7,78 (dd, 2H, J = 8.1, 2.0 Hz), 6.97-7.49 (m, 3H), 3.96 (brs, 1H), 2.21(s, 3H); MS (ES) calcd for $C_{14}H_{11}N_3O_2$ (M^+) *m/z* 253.25, found 253.17.

2-[3-fluoro-4-(trifluoromethyl)phenyl]-5-methyl-1*H*-benzimidazole (l): IR (KBr, cm^{-1}): ν 3235 (NH), 2967 (CH), 1641;^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.47-7.43 (m, 3H), 7.12-6.95 (m, 3H), 3.64 (brs, 1H), 2.28(s, 3H); MS (ES) calcd for $C_{15}H_{10}F_4N_2$ (M^+) *m/z* 294.24, found 294.20.

phenyl(2-phenyl-1*H*-benzimidazol-5-yl)methanone (m): IR (KBr, cm^{-1}): ν 3179 (NH), 2965 and 2916 (CH), 1709, 1641; ^{1}H NMR (200 MHz, $CDCl_3$/$DMSOD_6$): δ 7.93-6.75 (m, 13H), 4.51 (brs, 1H); MS (ES) calcd for $C_{20}H_{14}N_2O$ (M^+) *m/z* 298.35, found 298.21.

[2-(4-nitrophenyl)-1*H*-benzimidazol-5-yl](phenyl)methanone (n): IR (KBr, cm^{-1}): ν 3191 (NH), 2970 and 2912 (CH), 1714, 1647; ^{1}H NMR (200 MHz, $CDCl_3$/$DMSOD_6$): δ 8.27-8.13 (m, 3H), 7.81-7.72 (m, 6H), 7.45-7.38 (m, 3H), 4.70 (brs, 1H); MS (ES) calcd for $C_{20}H_{13}N_3O_3$ (M^+) *m/z* 343.33, found 343.25.

{2-[3-fluoro-4-(trifluoromethyl)phenyl]-1*H*-benzimidazol-5-yl}(phenyl)methanone (o): IR (KBr, cm^{-1}): ν 3180 (NH), 2967 and 2908 (CH), 1709, 1643; ^{1}H NMR (200 MHz, $CDCl_3$/$DMSOD_6$): δ 8.05 (s, 1H), 7.79-7.65 (m, 4H), 7.50-7.15 (m, 6H), 4.90 (brs, 1H); MS (ES) calcd for $C_{21}H_{12}F_4N_2O$ (M^+) *m/z* 384.32, found 384.27.

Acknowledgments

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