

One-Step Synthesis of Dicyano Imidazoles by $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6/\text{HNO}_3$ Promoted Oxidative Cyclocondensation of an Aldehyde and 2,3-diaminomaleonitrile

Kalhor, Mehdi*[†]; Seyedzade, Zahra

Department of Organic Chemistry, Payame Noor University, P.O. Box 19395-4697 Tehran, I.R. IRAN

ABSTRACT: The purpose of this study is to obtain a facile, mild, and effective synthetic method for the one-pot synthesis of 2-aryl-4,5-dicarbonitrile imidazole derivatives 3a-q from oxidative cyclocondensation of aromatic aldehydes and 2,3-diaminomaleonitrile (DAMN) by cerium(IV) ammonium nitrate/nitric acid (CAN/NA) as a novel and efficient oxidation catalyst. This synthetic protocol is cost-effective in addition to other advantages such as rapid transformation with good to excellent yields of products, one-step process and avoiding the pre-functionalization of the starting materials, simple workup procedure and easy operation under mild conditions in comparison previously report. These valuable conditions may be ideally suited for an effective synthesis of dicyano imidazole heterocycles on a larger scale.

KEYWORDS: One-step synthesis; Catalytic oxidation; Ceric ammonium nitrate (CAN)/ HNO_3 ; Diaminomaleonitrile; Dicyano imidazole.

INTRODUCTION

Imidazole and its derivatives are one of the most important and useful heterocycles among organic compounds. Imidazole rings are present in some natural products like alkaloids, in many fungicides, antiprotozoal, and antihypertensive medications such as clotrimazole, metronidazole and eprosartan, in biological building blocks for example histidine [1-3]. These important rings have also been used for industrial applications like corrosion inhibitor on certain transition metals, fire retardant, photography and electronics [4,5]. Salts of imidazole can also be found in the structure of various ionic liquids that are used for catalytic processes [6]. The structure of some of the drugs and biological molecules containing the imidazole ring is shown in Fig. 1.

Therefore, in recent years, considerable attention has been focused on the development of synthetic methods of substituted imidazoles and also the studies of their biological properties, and synthetic applications [7,8].

A number of substituted imidazoles, including 2-aryl-4,5-dicarbonitrile imidazoles have attracted much attention in medicinal chemistry and organic synthesis. Some of them have displayed pharmacological activities and have used in the synthesis of new promising acceptor moiety [9, 10]. There are a few methods for preparation of dicyanoimidazole heterocycles. So far, the four general synthetic methods including the use of Schiff bases and oxidant reagents have been reported [11-14]. The most previously methods have some disadvantages such as long

* To whom correspondence should be addressed.

+ E-mail: mekalhor@gmail.com

1021-9986/2020/6/1-8

8/\$/5.08

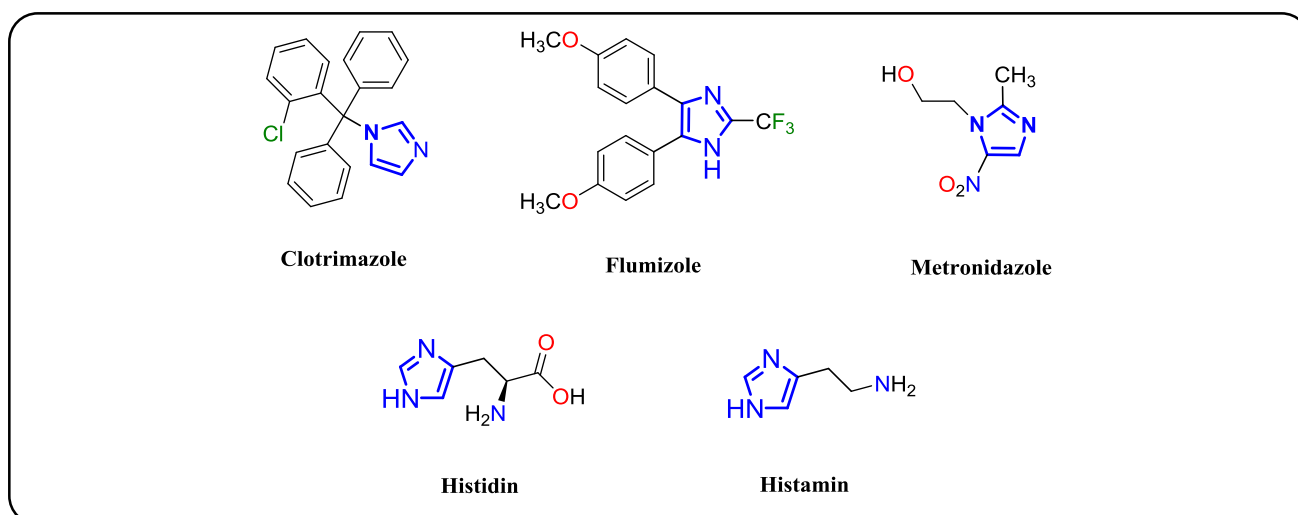


Fig. 1: Some of the drugs and biological molecules containing the imidazole ring.

reaction times, hazardous reaction conditions, the use of stoichiometric amounts of toxic reagents, tedious work-up and purification and low yield of products. Recently, it has been reported that the use of ceric ammonium nitrate (CAN) as a reagent is very effective for the synthesis of 2-aryl-4,5-dicyanitrile imidazoles. But the usage of excess amount of CAN reagent (0.45 equiv.) and one-pot, two-step procedure of this reaction is not a cost-effective strategy [15]. Therefore, the development of an efficient, cost-effective and high-yield synthetic protocol is required in the synthesis of dicyano imidazoles.

CAN is a valuable catalyst and multipurpose reagent for the synthesis of heterocycles such as tetrahydroindoles [16], tetrazole [17], chromenes [18], thiadiazoles [19], hydroxycoumarines [20], and indoles [21]. The extensive use of CAN as a catalyst and oxidant reagent is due to many advantages like air stable, inexpensive, excellent solubility in water and reasonably soluble in many organic solvents, eco-friendly nature, easy handling and high reactivity [23,24].

However, the use of CAN/HNO₃ mixture as a high oxidant catalyst in the one-step approach for preparation of 2-aryl-4,5-dicyanitrile imidazoles has not yet been explored. Therefore, in this investigation and in our further research efforts for the easy catalytic synthesis of heterocyclic compounds with valuable biological properties [25-28], we report for the first time, CAN/NA catalyzed synthesis of dicyano imidazoles by oxidative condensation of aromatic aldehyde with DAMN under mild conditions and high yield in comparison to previously reports.

EXPERIMENTAL SECTION

Chemical reagents in high purity were purchased from the Merck Chemical Company with commercial grade. Melting points were determined in open capillaries using an electro-thermal digital melting point apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded with a Bruker spectrometer (400 or 500 MHz). NMR spectra were obtained in DMSO-*d*₆ solution and are reported as parts per million (ppm) downfield from Me₄Si as internal standard. FT-IR spectra were obtained with potassium bromide pellets in the range 400-4000 cm⁻¹ with a JASCO 4200-A spectrometer. A mass spectrum was recorded by an Agilent model: 5975C VL MSD with a Triple-Axis detector spectrometer at 70 eV.

General one-pot procedure for the synthesis of dicyano imidazoles

A mixture of DAMN (0.5 mmol), aromatic aldehyde (0.5 mmol), and CAN/NA (0.05/0.4 equiv.) was heated at 70 °C in acetonitrile (2 mL), for desired time (Table 2). The reaction was followed by Thin Layer Chromatography (TLC) (ethyl acetate/*n*-hexane, 2:1). After the completion of reaction, the organic solvent was removed. The precipitate was dissolved in a small amount of ethanol and increasing some cold water results in pure product. Most of the dicyano imidazole products are known and were characterized by comparison of their physical (Mp) and spectral data (IR, ¹H NMR, and ¹³C NMR) with those of authentic samples.

2-(3-Chlorophenyl)-1H-imidazole-4,5-dicarbonitrile (3c)

FT-IR (KBr) (ν_{max}): 3436, 3179 (N-H), 3090 (C-H), 2261, 2234 ($\text{C}\equiv\text{N}$), 1644 ($\text{C}=\text{N}$), 1466 ($\text{C}=\text{C}$), 1120, 799 (C-Cl), 725 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ_{H} 7.56-7.59 (t br, 2H, H-Ar), 7.92 (d, $J = 6.85$ Hz, 1H, H-Ar), 7.98 (s, 1H, H-Ar), (NH of the imidazole ring was not observed that probably due to the effect of exchange of this acidic proton with deuterium in small amounts of D_2O , which is present in $\text{DMSO-}d_6$) ppm.

2-(2,3-Dichlorophenyl)-1H-imidazole-4,5-dicarbonitrile (3f)

FT-IR (KBr) (ν_{max}): 3289 (N-H), 2240 ($\text{C}\equiv\text{N}$), 1651 ($\text{C}=\text{N}$), 1541, 1506, 1446, 1417, 1308 ($\text{C}=\text{C}$), 1237, 1193, 1156, 1135, 1083, 1055, 975, 804 (C-Cl), 710, 500 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ_{H} 7.54 (t, $J = 7.92$ Hz, 1H, H-Ar), 7.72 (d, $J = 7.65$ Hz, 1H, H-Ar), 7.86 (d, $J = 8.00$ Hz, 1H, H-Ar) ppm, (NH of the imidazole ring was exchanged with D_2O); $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$): δ_{C} 111.1, 115.8, 128.6, 129.4, 130.1, 130.7, 132.7, 133.0, 148.1 ppm.

2-(4-Bromophenyl)-1H-imidazole-4,5-dicarbonitrile (3h)

FT-IR (KBr) (ν_{max}): 3442, 3171 (N-H), 3093 (C-H), 2258, 2234 ($\text{C}\equiv\text{N}$), 1600 ($\text{C}=\text{N}$), 1557, 1540, 1473, 1424 ($\text{C}=\text{C}$), 1010, 832 (C-Br), 728, 577 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ_{H} 7.77 (d, $J = 8.40$ Hz, 2H, H-Ar), 7.92 (d, $J = 8.40$ Hz, 2H, H-Ar) ppm, (NH of the imidazole ring was exchanged with D_2O).

2-(4-Nitrophenyl)-1H-imidazole-4,5-dicarbonitrile (3i)

IR (KBr) (ν_{max}): 3447 (N-H), 2232 ($\text{C}\equiv\text{N}$), 1605 ($\text{C}=\text{N}$), 1518, 1348 (NO_2), 1475 ($\text{C}=\text{C}$), 1112, 860, 716 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ_{H} 8.20 (d, $J = 8.40$ Hz, 2H, H-Ar), 8.33 (d, $J = 8.40$ Hz, 2H, H-Ar) ppm; EIMS (m/z , %): 239 (M^+ , 100), 209 (44), 181 (54), 139 (19), 102 (19), 75 (15), 50 (25).

2-(2-Methoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3k)

FT-IR (KBr) (ν_{max}): 3276 (N-H), 2238 ($\text{C}\equiv\text{N}$), 1603 ($\text{C}=\text{N}$), 1475 ($\text{C}=\text{C}$) 1247 (C-O), 1209, 1091, 1021, 749 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ_{H} 3.25 (s, 3H, OMe), 7.08-7.23 (m, 2H, H-Ar), 7.50 (d, $J = 4.40$ Hz, 1H, H-Ar), 8.04 (d, $J = 6.00$ Hz, 1H, H-Ar), 13.72 (br, 1H, NH) ppm; $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$): δ_{C} 55.7 (OMe), 111.1, 112.1, 115.3, 119.1, 121.0, 129.4, 132.6, 147.9 ($\text{C}=\text{N}$), 156.5 (C-O) ppm.

2-(2,5-Dimethoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3o)

FT-IR (KBr) (ν_{max}): 3277 (N-H), 2234 ($\text{C}\equiv\text{N}$), 1591 ($\text{C}=\text{N}$), 1543, 1490, 1438, 1307 ($\text{C}=\text{C}$), 1281, 1196 (C-O), 1171, 1146 (O-Me), 1084, 1042, 1018, 811, 743 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ_{H} 3.78 (s, 3H, OMe), 3.92 (s, 3H, OMe), 7.10 (dd, $J_1 = 2.90$ Hz, $J_2 = 6.15$ Hz, 1H, H-Ar), 7.17 (d, $J = 9.05$ Hz, 1H, H-Ar), 7.56 (d, $J = 2.80$ Hz, 1H, H-Ar), 13.72 (br, 1H, NH) ppm; $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$): δ_{C} 55.6, 56.0 (OMe), 111.3 (2C), 113.3, 115.6, 118.5 (2C), 147.9, 150.9, 153.1 ppm.

2-(3,4,5-Tri methoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3p)

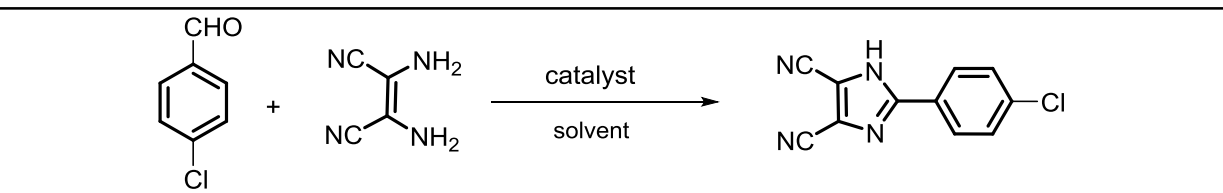
FT-IR (KBr) (ν_{max}): 3464, 3299 (N-H), 2939 (C-H), 2230, 2208 ($\text{C}\equiv\text{N}$), 1617 ($\text{C}=\text{N}$), 1584, 1508, 1382, 1332 ($\text{C}=\text{C}$), 1242, 1128 (C-O), 987 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ_{H} 3.71 (s, 3H, OMe), 3.83 (s, 6H, OMe), 7.25 (d, $J = 1.58$ Hz, 2H, H-Ar) ppm; $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$): δ_{C} 56.0, 60.2 (OMe), 103.6, 111.2, 122.5, 139.6, 145.4, 150.6, 153.3 (C-O) ppm.

RESULTS AND DISCUSSION

At the beginning of the research, the condensation of 4-chlorobenzaldehyde and DAMN as a model reaction with 0.4:5 eq. of CAN:NA as catalyst was carried out in different solvents, including EtOH, H_2O , MeCN and CH_2Cl_2 at $70\text{ }^\circ\text{C}$. The results are shown in Table 1. MeCN was chosen to be the best media for this condensation. Then, different amounts of CAN/NA were evaluated under similar condition and 0.05/0.4 eq. of CAN/NA was sufficient for completion of the reaction during 25 minutes with excellent yield. Furthermore, the use of 0.5 eq. of HNO_3 (without CAN) formed a number of by-products and decreased the yield of the product to 20%. Increasing 0.05 eq. of CAN in the absence of HNO_3 did not improve the yield. The use of HNO_3 as a co-oxidant was necessary in this CAN-catalyzed synthesis. When the model reaction was carried out with H_2O_2 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and CAN, the catalytic reaction was not successful.

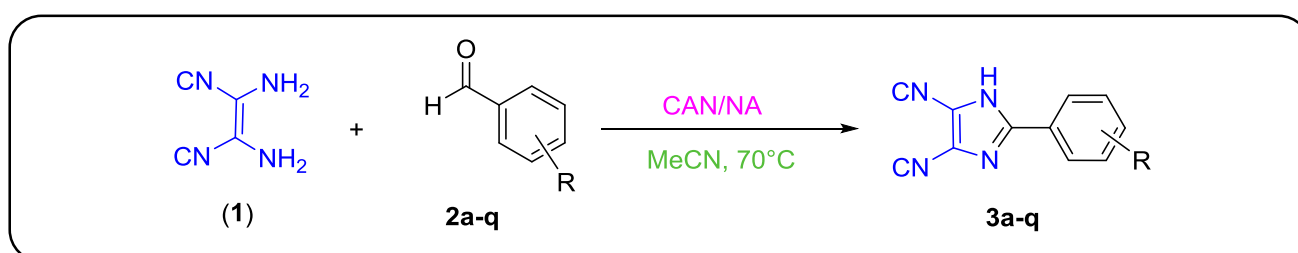
Importantly for the ultimate goal of applying the current method in a diversity-generating strategy, this catalytic procedure extended to the different kinds of aromatic aldehydes under similar conditions (Scheme 1).

Table 1: Optimization of reaction conditions for the synthesis of dicyano imidazoles at 70 °C.



Entry	Catalyst	Catalyst loading (equiv.)	Solvent	Reaction time (min)	Yield (%) ^a
1	CAN/NA	0.4/5	EtOH	120	25 ^b
2	CAN/NA	0.4/5	H ₂ O	120	0 ^b
3	CAN/NA	0.4/5	MeCN	20	85
4	CAN/NA	0.4/5	CH ₂ Cl ₂	120	0
5	CAN/NA	0.2/1	MeCN	35	85
6	CAN/NA	0.1/1	MeCN	30	88
7	CAN/NA	0.05/1	MeCN	20	88
8	CAN/NA	0.03/1	MeCN	40	30
9	CAN/NA	0.05/0.4	MeCN	25	92
10	CAN/NA	0.05/0.2	MeCN	60	0 ^c
11	HNO ₃	0.5	MeCN	120	0 ^b
12	CAN	0.05	MeCN	120	0 ^{b,c}
13	CAN/H ₂ O ₂	0.05/2	MeCN	60	0 ^c
14	CAN/APS ^d	0.05/0.1	MeCN	60	0 ^c
15	-	-	MeCN	120	0 ^b

a) Isolated yield. B) The reaction was performed under refluxing, also increase the catalyst up to 2 equiv. but no pure product was obtained.
c) The product was Schiff base. d) Ammonium per sulfate

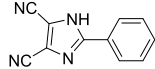
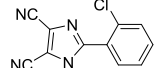
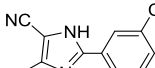
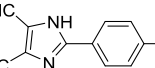
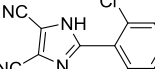
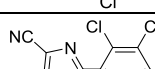
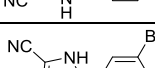
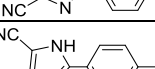
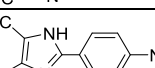
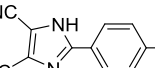
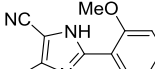
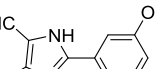
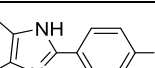
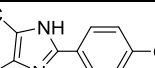
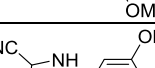
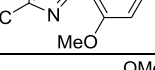
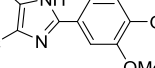


Scheme 1: The synthetic pathway of dicyano imidazoles.

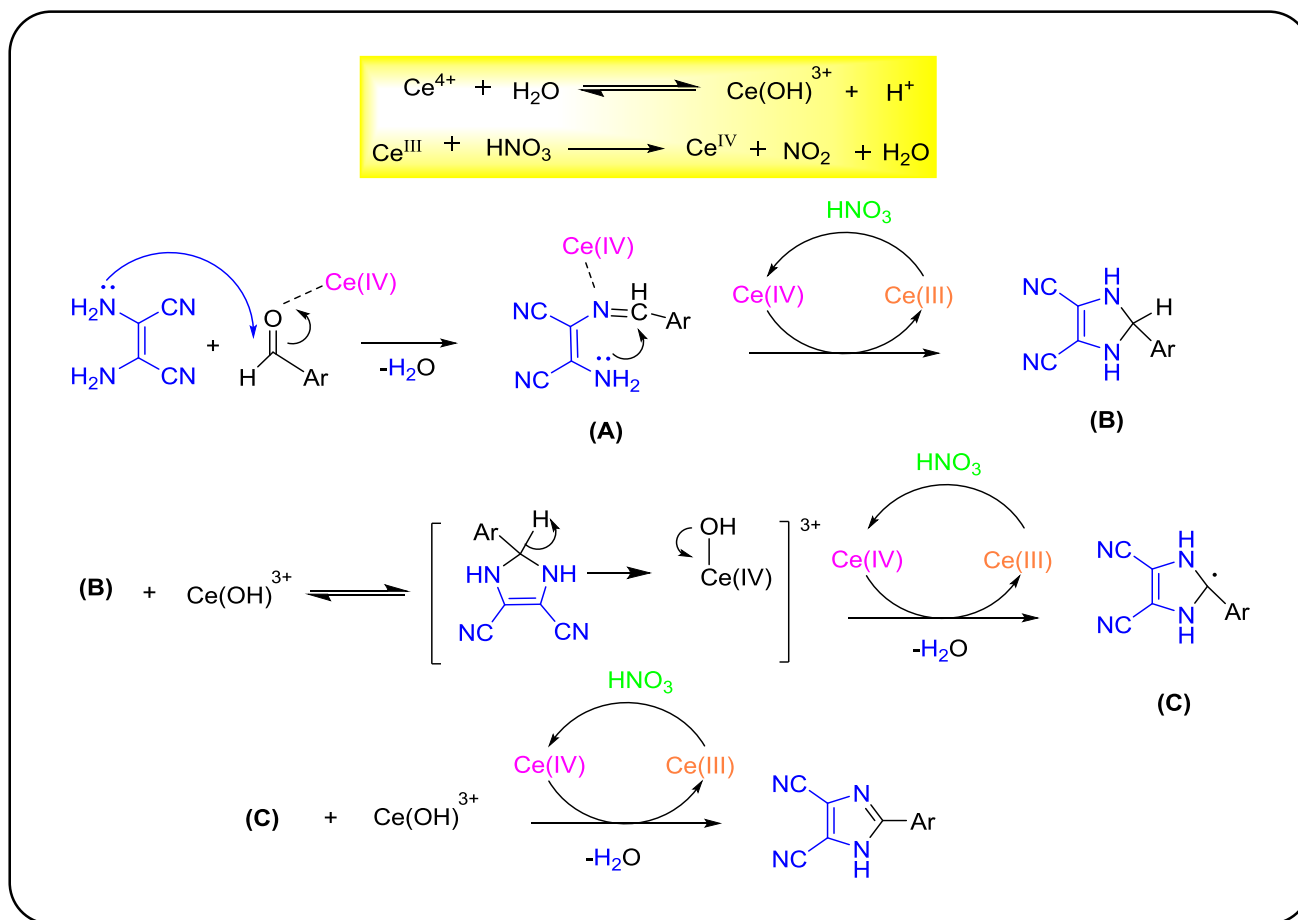
The experimental results are summarized in Table 2. As expected, the corresponding dicyano imidazoles were obtained in moderate to excellent yields with high purity for both electron-donating and electron-withdrawing substituents.

A plausible catalytic mechanism CAN/NA mediated synthesis of dicyano imidazoles is shown in Scheme 2. In this mechanism, CAN/NA system can act as a Lewis acid catalyst for activating the carbonyl group for synthesis of Schiff base. Moreover, CAN is a high efficient oxidant

Table 2: Synthesis of dicyano imidazoles catalyzed with CAN/NA in MeCN and at 70 °C.

No.	Product	Mp (°C) [Ref]	Reaction time (min)	Yield (%)
3a		219-220 (220-222) [12]	50	75
3b		204-206 (202-204) [15]	35	89
3c		218-220 227-228 [11]	35	78
3d		290-293 (288-290) [15]	25	92
3e		232-235 (233-235) [15]	40	76
3f		242-245	30	85
3g		225-227 212-213 [11]	35	82
3h		298-300 (316-321) [15]	30	92
3i		254 (252-254) [15]	30	89
3j		214-216 (211-212) [13]	35	85
3k		220-222 (223-225) [15]	30	85
3l		180-181 (173-177) [15]	45	80
3m		230-232 (230-232) [15]	20	95
3n		240 (238-241) [15]	30	93
3o		245-248	25	88
3p		243-245 (243-246) [15]	35	80
3q		228-230 (229-231) [15]	35	75

a) Isolated yields



Scheme 2: Plausible mechanism for the one-pot reaction in the presence of CAN/NA.

in the presence of HNO_3 . CAN generate $\text{Ce}(\text{OH})^{3+}$ as the reactive $\text{Ce}(\text{IV})$ species [29] that they are useful for closing the imidazole ring, which is an oxidative process. The present reaction had been previously carried out with an excess CAN (0.45 equiv.) in one-pot, two-step reaction [15], but it was completed successfully using catalytic amounts of CAN in one-step approach, when HNO_3 as co-oxidant was used. CAN was found to be inactive in itself (Ce^{+3}) for oxidative cyclocondensation, but it afforded excellent yields when the reaction was carried out in acidic conditions by addition of HNO_3 . Regeneration of the $\text{Ce}(\text{IV})$ catalyst was performed by HNO_3 [30].

Moreover, we compared results reported in the literature with this research method. The results are presented in Table 3. It is clear from this table that the one-step synthesis of dicyanoimidazoles performed using CAN/NA as a high activated oxidation catalyst under mild reaction conditions with excellent purity and high yield

in short reaction times and avoided the prefunctionalization of the aldehydes to Schiff bases.

CONCLUSIONS

In conclusion, we report a novel catalytic strategy and synthetic methodology that leads to the synthesis of dicyanoimidazoles starting from direct transformation DAMN and aldehyde derivatives by using CAN/NA catalytic system. The value of this approach in comparison to all previous methods was demonstrated in the one-pot and one-step reaction with available starting materials. The use of CAN/NA as a catalytic oxidation system can provide new way for continuous processes in the synthesis of heterocyclic compounds with diverse applications which so far were obtained in difficult conditions.

Acknowledgments

We gratefully acknowledge the financial support from the Payame Noor University for supporting this work.

Table 3: Comparison of conditions used for the synthesis of dicyano imidazole 3c.

Entry	Starting materials	Conditions	Yield (%) [Ref.]
1	Schiff bases ^a	DDQ ^b , MeCN, Reflux for 4 days	33 [11]
2	Schiff bases ^a	NCS ^c , nicotinamide DMF, 40°C, 3h	64 ^d [12]
3	Schiff bases ^a	Iodine, and sodium acetate, 1-methyl pyrrolidin-2-one, 100 °C, 24h	59 [13]
4	Schiff bases ^a	Pb(OAc) ₄ , Benzene, 5-10 °C, overnight	49 ^e [14]
5	Schiff bases ^a	CAN (0.40 eq.), MeCN, 50 °C, 40 min, two-step	84 [15]
6	DAMN, aldehyde	CAN/NA (0.05/0.4), MeCN, 70°C, 25 min, one-step	92, This work

a) Schiff bases from condensation of DAMN with aldehydes. b) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

c) N-chloro-succinimide . d) The yield of 3b. e) The yield of 2-Isopropyl-4,5-dicyanoimidazole

Received : Mar. 8, 2019 ; Accepted : Sep. 2, 2019

REFERENCES

- [1] Ali I., Lone, M.N., Aboul-Enein, H.Y., [Imidazoles as Potential Anticancer Agents](#), *Med. Chem. Commun.*, **8**: 1742-1773 (2017).
- [2] De Luca L., [Naturally Occurring and Synthetic Imidazoles: Their Chemistry and Their Biological Activities](#). *Curr. Med. Chem.*, **13**: 1-23 (2006).
- [3] Shargel L., Mutnick A.H., Souney P.F., Swanson L.N., "Comprehensive Pharmacy Review" (7th ed.), LWW, Amazon Business, U.S., ISBN: 9781582557113.
- [4] Yoshida S., Ishida H., [A Study on the Orientation of Imidazoles on Copper as Corrosion Inhibitor and Possible Adhesion Promoter For Electric Devices](#), *J. Chem. Phys.*, **78**: 6960-6969 (1983).
- [5] Hou Y., Hu W., Zhou X., Gui Z., Hu Y., [Vertically Aligned Nickel 2-Methylimidazole Metal–Organic Framework Fabricated from Graphene Oxides for Enhancing Fire Safety of Polystyrene](#), *Ind. Eng. Chem. Res.*, **56**: 8778-8786 (2017).
- [6] (a) Rani A., Rajoria P., Agarwal S., [Imidazolium chloride Immobilized Fly Ash as a Heterogenized Organocatalyst for Esterification Reaction under Microwave Irradiation Heating](#), *Iran. J. Chem. Chem. Eng.*, (*IJCCE*), **38**(3): 87-96 (2019);
 (b) Shaabani A., Mofakham H., Rahmati A., Farhangi E., [1-Butyl-3-methylimidazolium Bromide Promoted Selectively Oxidation of Sulfur Compounds by NaBrO₃](#). *Iran. J. Chem. Chem. Eng.* (*IJCCE*), **31**: 1-8 (2012).
- [7] (a) Kalhor M., zarnegar z., [Fe₃O₄/SO₃H@zeolite-Y as a Novel Multi-Functional and Magnetic Nanocatalyst for Clean and Soft Synthesis of Imidazole and Perimidine Derivatives](#), *RSC Adv.*, **9**: 19333-19346 (2019).
 (b) Safari J., Zarnegar Z., [Magnetic Nanoparticle Supported Ionic Liquid as Novel and Effective Heterogeneous Catalyst for Synthesis of Substituted Imidazoles Under Ultrasonic Irradiation](#), *Monatsh Chem.*, **144**: 1389-1396 (2013).
- [8] Amini Moghaddam Z., Behmadi H., Poormorteza N., Beyramabadi, S.A., Arian Nezhad, M., [A Four Components, One-Pot Synthesis of New Imidazole Molecular Tweezers Based on 2,4,6-Triarylpyridine as Hinge Region](#). *Iran. J. Chem. Chem. Eng.* (*IJCCE*), **36**: 11-17 (2017).
- [9] Wittine K., Babic M.S., Makuc D., Plavec J., Pavelic S.K., Sedic M., Pavelic K., Leyssen J.P., Neyts J., Balzarini J., Mintas M., [Novel 1,2,4-Triazole and Imidazole Derivatives of L-Ascorbic and Imino-Ascorbic Acid: Synthesis, Anti-HCV and Antitumor Activity Evaluations](#). *Bioorg. Med. Chem.*, **20**: 3675-3685 (2012).
- [10] Nepras M., Almonasy N., Bures F., Kulhánek J., Dvořák M., Michl M., [Fluorescence and Photophysical Properties of D-II-A Push-Pull Systems Featuring a 4,5-Dicyanoimidazole Unit](#), *Dyes Pigments*, **91**: 466-473 (2011).
- [11] Begland R.W., Hartter D.R., Jones F.N., Saw, D.J., Sheppard W.A., Webster O.W., Weigert F.J., [Hydrogen Cyanide Chemistry. VIII. New Chemistry of Diaminomaleonitrile. Heterocyclic Synthesis](#), *J. Org. Chem.*, **39**: 2341-2350 (1974).

- [12] Moriya O., Minamide H., Urata Y., **A Convenient Synthesis of 2-Aryl-4,5-Dicyanoimidazoles and -Imidazolines from Diaminomaleonitrile**, *Synthesis*, **12**: 1057-1058 (1984).
- [13] Feldwick G.A., Hatton L.R., Hewett R.H., Pedgrift B.L., **Imidazoles and Their Compositions for Plant Growth Regulation**. EP0269238 (1988).
- [14] Patel N.R., Kans S.M. **4, 5-Dicyanoimidazoles and Use as Herbicides**. US4220466 (1980).
- [15] Kalhor M., Seyedzade Z., **Rapid Synthesis of 2-Amino Maleonitrile Schiff Bases in Aqueous Media Catalyzed By Cerium(IV) Ammonium Nitrate (CAN) and a New Method for the One-Pot Preparation of Their Dicyano Imidazoles (DCI)**, *Res. Chem. Intermed.*, **43**: 3349-3360 (2017).
- [16] To Q.H., Lee Y.R., Kim S.H., **One-Pot Esterification and Amidation of Phenolic Acids**, *Tetrahedron*, **70**: 8108-8107 (2014).
- [17] Mitra B., Mukherjee S., Pariyar G.C., Ghosh P., **One Pot Three-Component Synthesis of 5-Substituted 1H-Tetrazole from Aldehyde**, *Tetrahedron Lett.*, **59**: 1385-1389 (2018).
- [18] Chitreddy S.V., Shanmugam S., **Solvent Free-Synthesis of Highly Functionalized 4H-Chromene-3-Carboxamide Derivatives Using Cerium Ammonium Nitrate and their Antioxidant, Antibacterial and Solvatochromism Studies**, *J. Mol. Liq.*, **243**: 494-502 (2017).
- [19] Vanajatha G., Reddy V.P., **High Yielding Protocol for Oxidative Dimerization of Primary Thioamides: a Strategy Toward 3,5-Disubstituted 1,2,4-Thiadiazoles**, *Tetrahedron Lett.*, **57**: 2356-2359 (2016).
- [20] Zaheer Z., Kalam Khan F.A., Sangshetti J.N., Patil R.H., **Expeditious Synthesis, Antileishmanial and Antioxidant Activities of Novel 3-Substituted-4-Hydroxycoumarin Derivatives**. *Chin. Chem. Lett.*, **27**: 287-294 (2016).
- [21] Tongkha, S., Radchatawedchakoon W., Kruanetr S., Sakee U., **Silica-Supported Ceric Ammonium Nitrate Catalyzed Chemoselective Formylation of Indoles**. *Tetrahedron Lett.*, **55**: 3909-3912 (2014).
- [22] Goswami P., Hazarika S., Das A.M., Chowdhury P., **Ceric Ammonium Nitrate (CAN) Catalyzed Baeyer-Villiger Oxidation of Carbonyl Compounds, Specially 20-Oxosteroids**, *Indian. J. Chem.*, **43B**: 1275-1281 (2004).
- [23] Prajapati N.P., Vekariya R.H. Patel H.D., **Ceric Ammonium Nitrate (CAN)-Catalyzed Multicomponent Reactions: An Efficient Catalyst for Green Organic Synthesis**. *Synth Commun.*, **45**: 2399-2425 (2015).
- [24] Sridharan V., Menéndez J.C., **Cerium(IV) Ammonium Nitrate as a Catalyst in Organic Synthesis**. *Chem. Rev.*, **110**: 3805-3849 (2010).
- [25] Mobinikhaledi A., Foroughifar N., Kalhor M., Mirabolfathy M., **Synthesis and Antifungal Activity of Novel 2-Benzimidazolylimino-5-Arylidene-4-Thiazolidinones**, *J. Heterocycl. Chem.*, **47**: 77-80 (2010).
- [26] Kalhor M., Mobinikhaledi A., Dadras A., Tohidpour M., **Synthesis and Antimicrobial Activity of Some Novel Substituted 1,2,4-Triazoles Bearing 1,3,4-Oxadiazoles or Pyrazoles**, *J. Heterocycl. Chem.*, **48**: 1366-1370 (2011).
- [27] Kalhor M., Dadras A., **Synthesis, Characterization, and Herbicidal Activities of New 1,3,4-Oxadiazoles, 1,3,4-Thiadiazoles, and 1,2,4-triazoles Derivatives Bearing (R)-5-Chloro-3-Fluoro-2-Phenoxy pyridine**, *J. Heterocycl. Chem.*, **50**: 220-224 (2013).
- [28] Kalhor M., seyedzade Z., **Ni@Zeolite-Y Nano-Porous: Preparation and Application as a High Efficient Catalyst for Facile Synthesis of Quinoxaline, Pyridopyrazine, and Indoloquinoxaline Derivatives**. *Iran. J. Chem. Chem. Eng.*, **50**: 27-41 (2019).
- [29] Mathur DL., Bakore G.V., **Kinetics of Oxidation of Cyclohexanol by Ceric Ammonium Nitrate in aq. HNO₃**, *Z. Naturforsch.*, **27b**: 46-49 (1972).
- [30] Johnson RW., Martin Jr D.S., **Kinetics of the Oxidation of Cerium(III) by Concentrated Nitric Acid**, *J. Inorg. Nucl. Chem.*, **10**: 94-102 (1959).