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Synthesis of 6-Amino-2, 4-Dihydropyrano-[2, 3-*c*]Pyrazol-5-Carbonitriles Catalyzed by Cerium(IV)carboxymethylcellulose under Solvent-Free Conditions

Ravindra M. Patil[1] and A. P. Rajput[2*]

1. Zulal Bhilajirao Patil College, Dhule, Dist. Dhule, Maharastra-424002, **INDIA**
2. K.K.Wagh Arts, Commerce, Science and Computer Science College, Saraswatinagar, Panchwati, Nashik-422003, **INDIA**

Email: aprajput@rediffmail.com, mr.raviraj86@rediffmail.com

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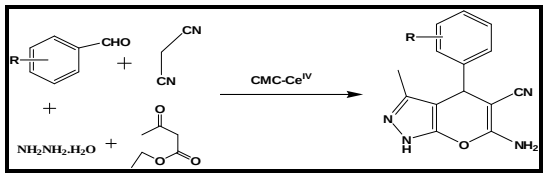
ABSTRACT

An efficient, high-yielding, and rapid protocol has been developed for the synthesis of 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles derivatives via a one-pot, four-component, reaction of hydrazinehydrate, ethyl acetoacetate, aldehydes, and malononitrile using Cerium(IV) carboxymethylcellulose as expeditious reusable heterogeneous catalyst. The protocol proves to be efficient and environmentally benign in terms of very easy workup, good yields, and ease of recovery of catalyst.

Graphical Abstract



Synthesis of 6-amino-4-aryl-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-carbonitriles catalyzed by CMC−Ce (IV)under solvent free conditions

Keywords: Heterogeneous catalyst, Cerium(IV) carboxymethylcellulose, Four-component reaction, pyrano[2,3-c]pyrazole.

INTRODUCTION

Multicomponent reactions (MCRs) play an important role in modern organic chemistry because they generally exhibit higher atom economy and selectivity as well as produce fewer by-products compared to classical multistep synthesis [**1**]. MCRs are easy to perform, inexpensive, and quick, consume less energy, and involve simple experimental procedures [**2**]. Dihydropyran [2,3-C]pyrazole moiety in their molecular framework have been reported as anticancer-antitumor [**3**], analgesic [**4**],

anti-inflammatory [5], antimicrobial [6], molluscicidal activities [7] and have been identified as a screening hit for Chk1 kinase inhibitor [8].

Otto first attempted, synthesis of 4H-pyrano [2,3-c] pyrazole from 3-methyl-3-pyrazolin-5-one and arylidene malononitrile using base catalyst [9]. There are several methods reported in the literature for the synthesis of 4H-pyrano [2,3-c]pyrazoles by using catalyst such as triethylamine [10], piperidine [11], morpholine [12], b-cyclodextrin [13], L-proline [14], acidic ionic liquid [15], tetra(n-butyl)ammonium bromide [16], P_2O_5-SiO_2 [17], $CeCl_3$ [18], and $NH_4H_2PO_4/Al_2O_3$ [19]. Several methods involving heterogeneous catalysts, such as amberlyst A21 [20], γ-alumina [21], and SnO_2 QDs [22], have been reported.

Recently, heterogeneous catalysts have been highly acknowledged for the sustainable development of any catalytic process because of their easy recovery, recyclability, minimization of undesired toxic wastes, and E factor [23]. The usage of heterogeneous metal Lewis acid catalyst instead of traditional homogeneous metal Lewis and Bronsted acid catalysts could be a more environmentally friendly alternative. Solid catalysts provide numerous opportunities for recovering and recycling catalysts from reaction environments [24].

Looking at these reactions, we decided to investigate efficiency of Cerium(IV)carboxymethylcellulose [25] heterogeneous catalyst for the synthesis of 6-amino-2,4-dihydropyrano [2,3-c]pyrazol-5-carbonitriles. Herein we report a one pot synthesis of 6-amino-2,4-dihydropyrano [2,3-c]pyrazol-5-carbonitriles derivatives from ethyl acetoacetate, hydrazine hydrate, aldehydes, and malononitrile using Cerium(IV) carboxymethylcellulose as expeditious reusable heterogeneous catalyst in an excellent yield (Scheme 1).

MATERIALS AND METHODS

Melting points was taken in open capillaries and are uncorrected. Progress of reaction was monitored by silica gel-G coated TLC plates in n-hexane: ethyl acetate system (9:1).The spot was visualized by exposing dry plate in UV chamber. IR spectra were recorded on Schimadu IR affinity model 1 spectrometer using KBr pellets.^{1}H NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance II 400 MHz NMR spectrometer (SAIF, Punjab University Chandigarh) in DMSO using TMS as internal standard. All reagents were obtained from commercial sources.

Typical Reaction procedure

Preparation of Cerium(IV) carboxymethylcellulose(CMC−Ce(IV)) Catalyst: The Cerium(IV) carboxymethylcellulose were prepared following the literature procedure [25]. The 5.5 wt.% aqueous solution of cerium(IV) ammonium nitrate (5.5 g dissolved in 94.5 mL H_2O) was slowly added drop wise to an aqueous 1.0 wt.% solution of sodium carboxymethylcellulose (1.0 g dissolved in 99 mL H_2O) with constant stirring at room temperature. Yellow solid was precipitated immediately which was left to equilibrate in solution for 12 h. The resulting solid was separated from the solution by suction and washed thoroughly with distilled water, then dried at 60◦C to constant weight to provide the CMC−Ce(IV) as yellow powder.

General Procedure for the Synthesis of 6-Amino-2, 4-dihydropyrano[2, 3-c]pyrazol-5-carbonitriles: A mixture of ethyl acetoacetate (2 mmol, 0.26 g), hydrazine hydrate(2 mmol, 0.12 g), aldehydes (2 mmol), malononitrile (2 mmol, 0.13 g) and CMC−Ce(IV) (10 mol%) was placed in a round bottom flask. The reaction mixture was stirred at room temperature under an open atmosphere for a specific time, as shown in table 1. Progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixtures as heated dissolve the product in ethanol and filtered hot. The filtrate was allowed to stand at room temperature when the product separated. It was filtered

and wash with water, followed by a mixture of ethyl acetate/hexane (20:80v/v), which was further purified by recrystallization with ethanol.

Spectral data of 6-Amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles

6-Amino-3-methyl-4-(p-tolyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1): White solid; m.p.: 172–175^{0}C, lit. [25] m.p.: 174–177^{0}C; IR (cm^{-1}): 3406(NH_2), 3331 (NH_2), 3219(NH), 2197 (CN), 2974 (C=C–H), 1467 (C=N), 1622 (C= C aromatic), 1190(C-O-C); 1H NMR (DMSO-d6, 400 MHz): δ_H:1.1 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.28 (s, 1H, CH=), 6.58 (br, s, 2H, NH_2), 7.02– 7.08 (m, 4H, Ar–H), 12.11 (s, 1H);^{13}C NMR (DMSO, 400 MHz): δ = 158, 156, 141, 135, 128.7, 127.02, 107, 59, 20.6, 13.6 ppm.

6-Amino-4-(4-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5carbonitrile(2): White solid; m.p.: 170–174^{0}C, lit. [25] m.p.: 172–176^{0}C; IR (cm^{-1}): 3400(NH_2), 3337 (NH_2), 3229(NH), 2201 (CN), 2982 (C=C–H), 1396 (C=N), 1598 (C= C aromatic), 1178(C-O-C); 1H NMR (DMSO-d6, 400 MHz): δ_H: 2.30 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 4.27 (s, 1H, CH=), 6.75 (br, s, 2H, NH_2),6.82(d, 2H, Ar–H), 7.09(d, 2H, Ar–H), 12.07 (s, 1H); ^{13}C NMR (DMSO, 400 MHz): δ = 165, 158, 155, 136.9, 136, 131, 129, 121, 114, 107, 59, 55.5, 13.6 ppm.

6-Amino-3-methyl-4-(4-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (3): White solid; m.p.: 194–196^{0}C, lit.[25] m.p.: 194–196^{0}C; IR (cm^{-1}): 3398(NH_2), 3329 (NH_2), 3217(NH), 2201 (CN), 2974 (C=C–H), 1364 (C=N), 1663 (C= C aromatic), 1064(C-O-C); 1H NMR (DMSO-d6, 400 MHz): δ_H: 2.38 (s, 3H, CH_3), 4.49 (s, 1H, CH=), 7.03 (br, s, 2H, NH_2),7.47(d, 2H, Ar–H), 8.20(d, 2H, Ar–H), 12.08 (s, 1H); ^{13}C NMR (DMSO, 400 MHz): δ = 164.9, 158, 157, 152, 146.3 128.7, 123.6, 119.2, 105, 60, 56, 40,13.6 ppm.

6-Amino-3-methyl-4-(2-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4): White solid; m.p.: 176–178^{0}C, lit.[25] m.p.: 178–180^{0}C; IR (cm^{-1}): 3445(NH_2), 3300 (NH_2), 3202(NH), 2210 (CN), 2980 (C=C–H), 1371 (C=N), 1604 (C= C aromatic), 1070(C-O-C); 1H NMR (DMSO-d6, 400 MHz): δ_H: 2.36 (s, 3H, CH_3), 5.08 (s, 1H, CH=), 6.96 (br, s, 2H, NH_2),7.45(m, 2H, Ar–H), 7.83(m, 2H, Ar–H), 12.05 (s, 1H); ^{13}C NMR (DMSO, 400 MHz): δ = 164.9, 158, 157, 148,139, 133 130, 128, 127, 123, 118, 106, 60, 56, 32, 13 ppm.

6-Amino-3-methyl-4-(m--tolyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5): White solid; m.p.: 152–154^{0}C, IR (cm^{-1}): 3383(NH_2), 3338 (NH_2), 3223(NH), 2191 (CN), 2960(C=C–H), 1398 (C=N), 1604 (C= C aromatic), 1060(C-O-C) ; 1H NMR (DMSO-d6, 400 MHz): δ_H:2.32 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 4.29 (s, 1H, CH=), 6.68 (br, s, 2H, NH_2),6.72– 6.77 (m, 4H, Ar–H), 12.05 (s, 1H); ^{13}C NMR (DMSO, 400 MHz): δ = 165.9, 159, 156, 146.3, 129, 119, 113, 111, 107, 59, 57, 54, 13 ppm.

6-Amino-4-(3,4-dimethoxylphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (6): White solid; m.p.: 174^{0}C, lit.[11] m.p.: 176–178^{0}C; IR (cm^{-1}): 3450(NH_2), 3337 (NH_2), 3109 (NH), 2222 (CN), 2943 (C=C–H), 1446 (C=N), 1575 (C= C aromatic), 1155(C-O-C); 1H NMR (DMSO-d6, 400 MHz): δ_H:2.52 (s, 3H, CH_3), 3.86 (s, 6H, OCH_3), 3.36 (s, 1H, CH=), 8.58 (br, s, 2H, NH_2), 7.02 (d, 1H, Ar–H), 7.34 (dd, 1H, Ar–H), 7.49 (d, 1H, Ar–H), 12.07 (s, 1H).^{13}C NMR (DMSO, 400 MHz): δ = 160.5, 151, 148, 126, 123, 111.1, 108, 55.5, 13 ppm.

6-Amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7): White solid; m.p.: 168^{0}C, lit.[25] m.p.: 164–167^{0}C; IR (cm^{-1}): 3391(NH_2), 3335 (NH_2), 3217(NH), 2189 (CN), 3061 (C=C–H), 1398 (C=N), 1612 (C= C aromatic), 1066(C-O-C) ; 1H NMR (DMSO-d6, 400 MHz): δ_H:1.4 (s, 3H, CH_3), 4.10 (s, 1H, CH=), 6.65 (br, s, 2H, NH_2), 7.44– 7.20 (m, 5H, Ar–H), 12.01 (s, 1H), ppm.

6-Amino-4-(4-chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile(8):
White solid; m.p.: 160^{0}C, lit.[25] m.p.: 158–160^{0}C; IR (cm^{-1}): 3406(NH_2), 3331 (NH_2), 3219(NH), 2193 (CN), 2987 (C=C–H), 1465 (C=N), 1681 (C= C aromatic), 1060(C-O-C) ; 1H NMR (DMSO-d6, 400 MHz): δ_H:1.83 (s, 3H, CH_3), 4.52 (s, 1H, CH=), 6.09 (br, s, 2H, NH_2), 7.22(d, 2H, Ar–H), 7.85 (d, 2H, Ar–H), 12.14 (s, 1H) ppm.

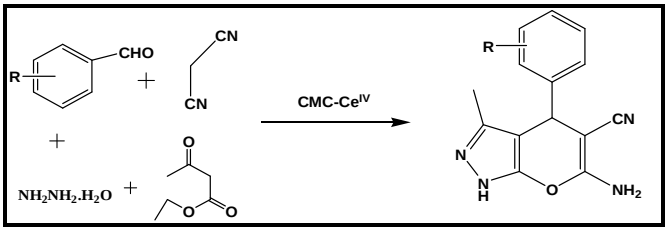
RESULTS AND DISCUSSION

To the best of our knowledge, this are the first examples of the use of Cerium(IV) carboxymethylcellulose (CMC−Ce ^{IV}) catalyst for the synthesis of 6-Amino-2,4-dihydropyrano[2,3-c] pyrazol-5-carbonitriles. The studies were initiated to optimize the reaction conditions for a model reaction of hydrazine hydrate, ethyl acetoacetate, benzaldehyde, and malononitrile in the presence of different mol% of catalyst (Table 1). To establish the real effectiveness of the catalyst for the synthesis of 6-amino-3-methyl-4-(3-phenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile, a test reaction was performed without catalyst using hydrazine hydrate, ethyl acetoacetate, benzaldehyde,

Table 1. Synthesis of 6-amino-4-aryl-3-methyl-2, 4-dihydropyrano [2, 3-c]pyrazole-carbonitriles catalyzed by CMC−Ce^{IV} .

Entry	CMC−Ce^{IV} (mol %)	Time (min)	Yield (%)
1	No catalyst	90	30
2	5	20	76
3	10	10	92
4	15	15	87
5	20	20	85

and malononitrile. It was found that only 30% yield of product was obtained in the absence of catalyst even after 1.5 h. To develop a viable approach, the model reaction was investigated by employing different mol% of CMC−Ce^{IV} catalyst. Moreover, we found that the yields were obviously affected by the amount of CMC−Ce^{IV} loaded (Table-1).



Scheme 1. Synthesis of 6-amino-4-aryl-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-carbonitriles catalyzed by CMC−Ce^{IV} under solvent free conditions.

Table 2. CMC−Ce^{IV} catalyzed synthesis of 6-amino-4-aryl-3-methyl-2,4-dihydropyrano [2,3-c]pyrazole-carbonitriles

Entry	R	Time(min)	Yield (%)
1	4-CH_3	10	86
2	4-OCH_3	13	84
3	4-NO_2	10	92
4	3-NO_2	15	84
5	3-OCH_3	12	85
6	3,4-$(OCH_3)_2$	15	86
7	H	10	92
8	4-Cl	12	89

Therefore, 10 mol% of CMC−Ce^{IV} was sufficient and optimal quantity for the completion of the reaction. By using this criteria, present study describe the synthesis of series of 6-amino-4-aryl-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-carbonitriles from hydrazine hydrate, ethyl acetoacetate, benzaldehyde and malononitrile catalyzed by CMC−Ce^{IV} under solvent free conditions (Scheme- I). The results of CMC−Ce^{IV} catalyzed synthesis of 6-amino-4-aryl-3-methyl-2,4-dihydropyrano[2,3-c] pyrazole-carbonitriles are presented in table 2. The structure of compounds 1–8 was deduced from their infrared spectral, ^{1}H NMR, and ^{13}CMR data. Also, their melting points were compared with literature reports.

APPLICATION

These investigations involve use of solvent free method. The procedure offers advantages in terms of better yields, short reaction times, mild reaction conditions, and reusability of the catalyst. The low cost, and ready availability of catalyst, an environmentally benign procedure makes this methodology, a useful contribution to the existing procedures available for the synthesis of pyranopyrazole derivatives as a biologically and pharmaceutically relevant materials.

CONCLUSIONS

In conclusion, a novel one-pot four-component synthesis in the presence of cerium carboxymethylcellulose (CMC−Ce^{IV}) and reusable catalyst under solvent-free condition has been developed. To the best of our knowledge, this is the first example of used of CMC−Ce^{IV} for the synthesis of these pyranopyrazole derivatives under solvent-free conditions. Present methodology offers very attractive features such as cleaner reaction profile, high efficiency, shorter reaction times, higher yields, and tolerance of wide scope of substrates which make the process efficient and practical. Simplicity, making it an attractive alternative for the clean synthesis of pyranopyrazole derivatives as a biologically and pharmaceutically relevant material.

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