

Cerium (IV) Ammonium Nitrate (CAN) Mediated Reactions IV. A Highly Efficient Synthesis of N,N'-Diarylsubstituted Formamidines in Water at Ambient Temperature

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Abstract

A green, simple and highly efficient synthesis of N,N-diarylsubstituted formamidines has been developed employs reaction of triethylorthoformate (TEO) with aromatic amines catalyzed by cerium (IV) ammonium nitrate (CAN) in water at ambient temperature. This method offers the advantages of proceeding under environmentally friendly technique with high yields and simplicity either in conducting the reaction or handling the products.

Keywords: CAN, Triethylorthoformate, Aromatic Amines, Water, Ambient Temperature

1. Introduction

Formamidines are of considerable interest in fields related to organic and medicinal chemistry. They act as starting materials in several synthetic approaches mainly in the synthesis of heterocycles [1-5]. Moreover, amidines were considered as precursors of acid functions [6,7] Furthermore, they possess antimalarial activity [8] which is effective against chloroquino-resistant strain [9]. Classes of compounds containing amidine structures have found enormous applications as building blocks in polymer synthesis [10,11], bleaching agents for paper [12], ultraviolet light absorbers [13], protecting groups for primary amines [14,15] and other several applications [16-19].

Many of known methods for the synthesis of formamidines require long reaction times and/or a multi-step procedures. Thus, Taylor *et al.* [15] have reported a general synthetic method for the synthesis of formamidines by the reaction of triethylorthoformate or orthoacetate with a number of aliphatic and aromatic amines in acetic acid under reflux at 140°C - 150°C for 1.5 - 94 hours.

Although the reduction of carbodiimides with sodium borohydride in isopropanol perform a convenient synthetic method of the corresponding formamidines [20] but this protocol suffers from the use of toxic organic solvents either in conducting the reaction or working-up the product. The exchange of N,N-dimethylformamidines or acetamidines by a variety of amines has been reported to be the most popular method for the synthesis of symmetrical and unsymmetrical formamidines [21]. This approach suffers from drawbacks of high temperatures and the use of protic organic solvents (mostly methanol or ethanol) for a period of 1 - 48 hours [22]. The beneficial effect of base in non-protic solvents for this transformations has also been reported [23]. A revisiting of the effect of acid in the amine exchange of N,N-dimethylformamidines has been recently reported [18] which allowing the preparation of highly electron-rich compounds that are difficult to obtain under standard conditions. In their study, they have claimed that such exchange is highly dependent on the nucleophilicity of the corresponding amine (e.g. weak nucleophiles such as aniline did not react at all and pyrrolidine gave a poor

yield). They also emphasized that, minor products derived from loss of the imine component rather than dimethylamine, followed by addition exchange reactions can often be observed. Unexpected formation of N,N' -disubstituted formamidines by the reaction of an amine with sodium hydride and trifluoroacetic anhydride in dimethylformamid has been recently reported [24]. Accordingly, the development of a simple, high yield and green protocol for the synthesis of such scaffold will be of interest for researches and scientists in such area.

Cerium (IV) ammonium nitrate (CAN) is a convenient and widely used catalyst for affecting a broad spectrum of synthetic transformations for its many advantages such as solubility in water, inexpensiveness, eco-friendly nature, simplicity in handling and convenient work-up which make CAN an interesting and potential catalyst in organic synthesis [25]. Although, the utility of CAN as a one-electron oxidant was extensively utilized in literature [26,27] its use as a Lewis acid catalyst in C-N bond formation is somehow limited [28]. In this connection, it is worth mentioning that CAN is a useful alternative to the expensive lanthanide triflates. Also, Ce salts are the ones that have the lowest affinity for oxygen, making them potential complementary to other extensively studied Lewis acids [29].

In continuation to our efforts utilizing a simple and green technologies for organic synthesis [30] we reported herein, for the first time, a convenient, green, highly efficient synthesis of N,N' -diarylsubstituted formamidines in water at ambient temperature performing CAN in catalytic amount.

2. Results and Discussion

With the aim of optimizing experimental conditions, we initially explored the reaction of aniline (**1a**) (1 mol) and triethylorthoformate (**2**) (1 mol) in water (20 mL) in the presence of CAN (10 mol%) at ambient temperature (27°C). The reaction was promoted by stirring for 15 minutes after which a solid was formed affording N,N' -diphenylformimidamide (**3a**), in moderate yield (60%). Upon duplication of aniline molar ratio the yield was highly improved up to 93%. We also explored the effect of catalyst molar ratio on overall yield. Our investigations clearly revealed that addition of (10 mol%) of CAN to the reaction mixture containing 2:1 molar ratios of amine **1** and triethyl-orthoformate (**2**) in water at ambient temperature was optimal for the formation of the target molecule **3**. Finally, irrespective of the aryl substituent, reactions utilizing a variety of aromatic amines took place in reasonable yields (**Table 1**).

In order to extend the scope of the reaction, heterocyclic amine **1h** was examined and the reaction proceeds easily with a good yield. However, attempted conden-

Table 1. Synthesis of N,N' -diarylsubstituted formamidines **3a-h** from aromatic and heterocyclic amines and triethylorthoformate^a.

Entry	Ar	Time (min.)	Yield (%) ^b
1	C ₆ H ₅ (1a)	15	3a , 93
2	<i>o</i> -MeC ₆ H ₄ (1b)	12	3b , 94
3	<i>p</i> -MeOC ₆ H ₄ (1c)	10	3c , 95
4	<i>p</i> -NO ₂ C ₆ H ₄ (1d)	40	3d , 86
5	<i>o</i> -ClC ₆ H ₄ (1e)	18	3e , 88
6	<i>p</i> -ClC ₆ H ₄ (1f)	18	3f , 87
7	<i>p</i> -BrC ₆ H ₄ (1g)	17	3g , 88
8	3-Methyl-pyrazol-4-yl (1h)	5	3h , 90

sation of aliphatic amines and triethylorthoformate was unsuccessful. Starting materials were recovered even after prolonged stirring. This may be rationalized for the fact that the equilibrium position for the reaction of an aliphatic amines with triethylorthoformate is probably in favor of the starting materials. Although, *syn-anti* isomerization is possible but the *anti*-isomer was favored based on the fact that *syn*-isomer is being sterically crowded²¹ (**Scheme 1**).

A proposed mechanism for the formation of **3** is shown in **Scheme 2**. It is clear from the sequence of steps that CAN as a Lewis acid activate ethoxy groups and enhance the C-O bond cleavage to generate carbenium ions that are stabilized by resonance facilitating subsequent nucleophilic displacements by aromatic amines.

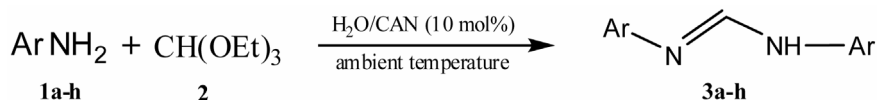
3. Conclusions

In conclusion, we have developed, for the first time, a convenient synthesis of N,N' -diarylsubstituted formamidines in water at ambient temperature catalyzed with (CAN). On the basis of the experimental results in our study, this annulations reaction proved to be green, simple and highly efficient procedure for the target molecules which make it a useful and important addition for such area of research.

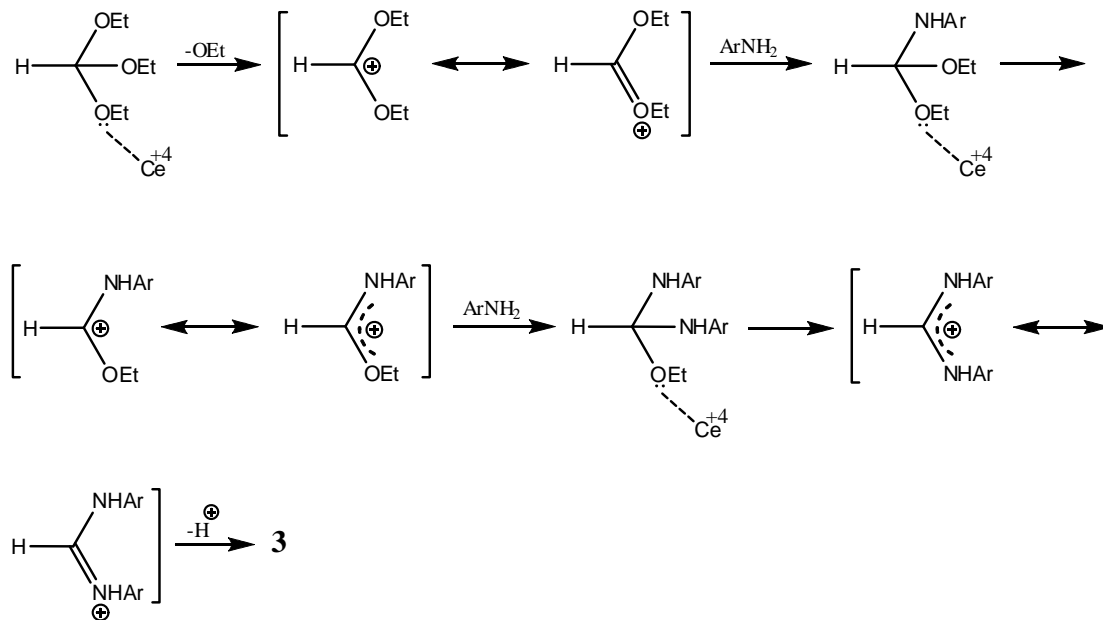
4. Experimental Section

4.1. General Procedures

Commercially available chemicals were used as received. IR spectra were recorded with a Shimadzu 470 spectrophotometer in KBr disks. The ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) were run on a Bruker DPX spectrometer with DMSO-*d*₆ as solvent and TMS as an internal standard; Chemical shifts (δ) were reported in ppm. Mass spectra were measured on VG Autospec Q MS 30 and MS 9 (AEI) spectrometers with EI 70 ev. Elemental an-



Scheme 1



Scheme 2

alyses were performed by using of LECO CHNS-932 Elemental Analyzer. Melting points were measured on a Gallenkamp apparatus in open capillary tubes. The purity of the products was checked by TLC (Merck Kieselgel 60 F₂₅₄)

4.2. Experimental Section

4.2.1. General Procedure for the Synthesis of N,N'-Disubstituted Formamidines 3a-h

To a stirred mixture of each of aromatic or heteroaromatic amines **1a-f** (20 mmol), triethyl-orthoformate (10 mmol) in water (20 mL) was added cerium (IV) ammonium nitrate (10 mol%). The reaction mixture was stirred at room temperature (27°C) for 10 - 40 minutes. For liquid amines a solid was formed, while for solid amines, they dissolved in the reaction medium and then re-solidified forming the final product. The resulting solid was collected by filtration and recrystallized from ethanol to afford analytically pure samples **3a-h**. Compounds **3a-f** have been described previously [31-37] and were found identical with our samples synthesized by our protocol.

4.2.2. N,N'-Diphenylformimidamide (3a)

Pale yellow crystals 0.183 g, 93% yield; mp 142°C -

143°C. IR (KBr pellet): 3422 (NH), 3050 (arom.CH), 1665 (C=N) cm⁻¹; MS: *m/z* (%) = 197 (M⁺ + 1, 8), 196 (M⁺, 69), 195 (25), 119 (3), 104 (15), 93 (100), 77 (42), 66 (7), 65 (7); ¹H NMR (DMSO-*d*₆, 400MHz): 9.70 (s, 1H), 8.27 (s, 1H), 7.39 - 6.90 (m, 10H). ¹³C NMR (DMSO-*d*₆, 100 MHz): 163.2, 152.6, 144.4, 130.1, 129.5, 127.2, 122.6, 122.3, 115.7. Anal. Calcd. for C₁₃H₁₂N₂ (196.1): C, 79.56%; H, 6.16%; N, 14.27%. Found: C, 79.44%; H, 6.11%; N, 14.31%.

4.2.3. N,N'-Bis(2-Tolylformimidamide) (3b)

Buff crystals 0.210 g, 94% yield; mp 161°C - 162°C. IR (KBr pellet): 3439 (NH), 3018 (arom. CH), 2939 (aliph. CH), 1662 (C=N) cm⁻¹; MS: *m/z* (%) = 225 (M⁺ + 1, 10), 224 (M⁺, 62), 223 (M⁺ - 1, 12), 209 (13), 133 (3), 118 (30), 107 (100), 91 (24), 65 (10); ¹H NMR (DMSO-*d*₆, 400 MHz): 8.76 (s, 1H), 7.80 (s, 1H), 7.05 (m, 5H), 6.85 (m, 3H), 2.41 (s, 3H), 2.17 (s, 3H). Anal. Calcd. C₁₅H₁₆N₂ (224.30): C, 80.32%; H, 7.19%; N, 12.49%. Found: C, 80.44%; H, 7.13%; N, 12.31%.

4.2.4. N,N'-Bis(4-Methoxyphenyl) Formimidamide (3c)

Colourless crystals 0.243 g, 95% yield; mp 254°C - 255°C. IR (KBr pellet): 3426 (NH), 3060 (arom. CH), 2925 (aliph. CH), 1663 (C=N) cm⁻¹; MS: *m/z* (%) = 257 (M⁺ + 1, 10), 256 (M⁺, 63), 134 (16), 123 (100), 108 (82),

77 (10); ^1H NMR (DMSO- d_6 , 400 MHz): 8.17 (br, 2H), 7.32 (d, $J = 7$ Hz, 2H), 6.94 (d, $J = 7$ Hz, 2H), 6.80 (d, $J = 8$ Hz, 2H), 6.74 (d, $J = 7$ Hz, 2H), 3.68 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (DMSO- d_6 , 100 MHz): 163.2, 159.3, 153.2, 144.7, 136.6, 122.1, 117.6, 115.5, 115.1, 55.7, 55.3. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$ (256.3) C, 70.29%; H, 6.29%; N, 10.93%. Found: C, 70.31%; H, 6.13%; N, 10.88%.

4.2.5. N_2N^- -Bis(4-Nitrophenyl)Formimidamide (3d)

Greenish crystals 0.233 g, 86% yield; mp $144^\circ\text{C} - 145^\circ\text{C}$. IR (KBr pellet): 3422 (NH), 3040 (arom. CH), 1668 (C=N) cm^{-1} ; MS (M^+) = 271.1; ^1H NMR (DMSO- d_6 , 400 MHz): 9.72 (s, 1H), 8.09 (s, 1H), 7.36 - 7.02 (m, 8H). Anal. Calcd for $\text{C}_{13}\text{H}_6\text{N}_3\text{O}_4$ (271.35): C, 54.55%; H, 3.52%; N, 19.57%. Found: C, 54.52%; H, 3.49%; N, 19.58%.

4.2.5. N_2N^- -Bis(2-Chlorophenyl)Formimidamide (3e)

Buff crystals 0.233 g, 88% yield; mp $148^\circ\text{C} - 149^\circ\text{C}$. IR (KBr pellet): 3439 (NH), 3050 (arom. CH), 1664 (C=N) cm^{-1} . MS: m/z (%) = 266 (M^+ , 13), 265 (M^+ , 5), 264 (M^+ , 18), 229 (35), 140 (5), 138 (14), 127 (100), 111 (18), 75 (10), 65 (3); ^1H NMR (DMSO- d_6 , 400 MHz): 9.16 (s, 1H), 8.45 (s, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.02 (m, 3H), 6.96 (t, $J = 8.4$ Hz, 3H). Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{N}$ (264.14): C, 58.89%; H, 3.80%; N, 10.57%; Cl, 26.74%. Found: C, 58.82%; H, 3.78%; N, 10.66%; Cl, 26.55%.

4.2.6. N_2N^- -Bis(4-Chlorophenyl)Formimidamide (3f)

Redish crystals 0.230 g, 87% yield; mp $185^\circ\text{C} - 186^\circ\text{C}$. IR (KBr pellet): 3420 (NH), 3014 (arom. CH), 1660 (C=N) cm^{-1} . MS: m/z (%) = 266 (M^+ , 49), 265 (M^+ , 17), 264 (M^+ , 79), 140 (7), 138 (25), 127 (100), 111 (35), 99 (8), 75 (16); ^1H NMR (DMSO- d_6 , 400 MHz): 9.79 (s, 1H), 8.09 (s, 1H), 7.26 - 7.08 (m, 8H). Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{N}_2$ (264.14): C, 58.89%; H, 3.80%; N, 10.57%; Cl, 26.74%. Found: C, 58.82%; H, 3.78%; N, 10.66%; Cl, 26.55%.

4.2.7. N_2N^- -Bis(4-Bromophenyl)Formimidamide (3g)

Buff crystals 0.311 g, 88% yield; mp $188^\circ\text{C} - 189^\circ\text{C}$. IR (KBr pellet): 3437 (NH), 3051 (arom. CH), 1660 (C=N) cm^{-1} . MS: m/z (%) = 356 (M^+ , 18), 354 (M^+ , 38), 352 (M^+ , 19), 182 (12), 171 (100), 155 (18), 92 (11), 76 (12), 64 (7); ^1H NMR (DMSO- d_6 , 400 MHz): 9.82 (s, 1H), 8.10 (s, 1H), 7.36 - 6.98 (m, 8H). Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{Br}_2\text{N}_2$ (354.04): C, 44.10%; H, 2.85%; N, 7.91%; Br, 45.14%. Found: C, 44.21%; H, 2.78%; N, 7.88%; Br, 45.23%.

4.2.8. N_2N^- -Bis(5-Methyl-1H-pyrazol-3-yl)Formimidamide (3h)

Pink crystals 0.178 g, 88% yield; mp $282^\circ\text{C} - 283^\circ\text{C}$. IR

(KBr pellet): 3422 (NH), 3015 (arom. CH), 2935 (aliph. CH), 1660 (C=N) cm^{-1} . ^1H NMR (DMSO- d_6 , 400 MHz): 12.66 (s, 1H), 12.23 (s, 1H), 9.15 (s, 1H), 8.08 (s, 1H), 2.35 (s, 3H), 2.30 (s, 3H). Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{N}_6$ (204.23): C, 52.93%; H, 5.92%; N, 41.15%. Found: C, 52.89%; H, 5.91%; N, 41.23%.

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