Ammonium Metavanadate As an Efficient Catalyst for the Synthesis of 2,4,5-Triaryl-1*H*-imidazoles

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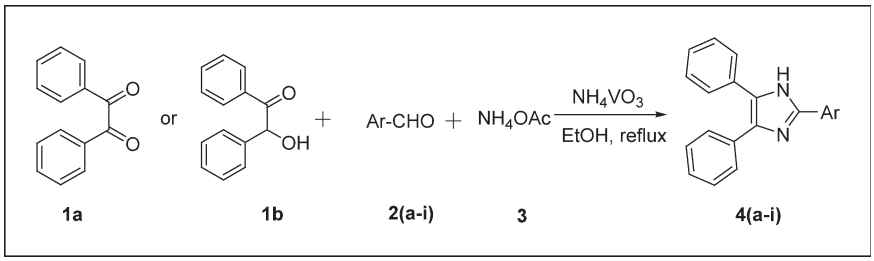

Ammonium metavanadate (NH_4VO_3) is an inexpensive, efficient and mild catalyst for the synthesis of 2,4,5-triaryl-1*H*-imidazole from the one-pot three-component condensation of benzil/benzoin, an aldehyde and ammonium acetate in excellent yield. This method has the advantages of good yield, green catalyst, simple procedure, much faster reactions.

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INTRODUCTION

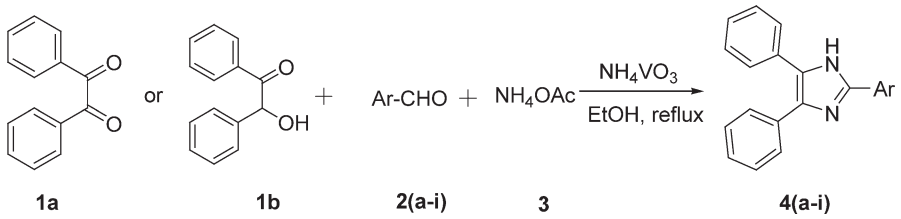
Imidazole derivatives are a very interesting class of heterocyclic compounds because they are found in many natural products and pharmacologically active compounds, such as antiulcerative agent cimetidine [1], the proton pump inhibitor omeprazole [2], and the benzodiazepine antagonist flumazenil [3], are imidazole derivatives. Many of the substituted imidazoles are known as inhibitors of p^{38} MAP kinase, fungicides, herbicides, plant growth regulators, and therapeutic agents.[4–7]. Owing to the wide range of pharmacological and biological activities, the synthesis of imidazoles has become an important target in current years. Methods for the synthesis of imidazoles include a four-component condensation using Wang's resin in refluxing acetic acid [8] and condensation of 1,2-diketones, aldehydes, primary amines, and ammonium acetate in phosphoric acid [9] and acetic acid [10] using an organocatalyst in acetic acid [11] and H_2SO_4 [12] and dimethyl sulfoxide (DMSO) [13]. A number of synthetic methods were reported for the synthesis of 2,4,5-triaryl-1*H*-imidazoles from the three-component condensation of benzil/benzoin, aldehydes, and ammonium acetate using various catalysts, such as ionic liquid [14], iodine [15], zeolite HY/silica gel [16], $ZrCl_4$ [17], acidic Al_2O_3 [18], AcOH [19], NH_4OAc [20], $Yb(OTf)_3$ [21], Scolecite [22], PEG-400 [23], L-proline [24], boric acid [25], and CAN [26]. However, most of these methods have one or more disadvantages, such as harsh reaction conditions, prolonged time period, poor yields, use of hazardous, and expensive catalysts. So the development of clean, high-yielding, and environmentally friendly approaches is still desirable and much in demand. The use of ammonium metavanadate (NH_4VO_3) as an inorganic acid [27] that meets the demand for an economic catalyst. It is employed similar to vanadium pentoxide [28] and as a catalyst in oxidation reactions with other cocatalysts [29]. It is a reagent used in analytical chemistry, the photographic industry, and the textile industry [28]. Jadhav and coworkers [30] reported the synthesis of benzimidazole in the presence of ammonium metavanadate. Very recently, we have reported [31] the synthesis of α-hydroxyphosphonates using ammonium metavanadate as a catalyst in good yields. In continuation [32] of our research work devoted to the development of useful synthetic methodologies for the synthesis of bioactive heterocycles, herein, we would like to report the facile and ecofriendly methodology for the synthesis of 2,4,5-triaryl-1*H*-imidazoles.

RESULTS AND DISCUSSION

The present method involves a cyclocondensation of Benzil **1a** with aromatic or heteroaromatic aldehydes **2**(**a**–**i**) and ammonium acetate **3** in ethanol using 10 mol % NH_4VO_3 as a catalyst resulted into the corresponding 2,4,5-triaryl-1*H*-imidazoles **4**(**a**–**i**) in good to excellent yield as indicated in Scheme 1.

Initially, we have studied the solvent effect for the synthesis of **4a** as a model reaction by reacting benzil

Scheme 1



1a, benzaldehyde **2a**, and ammonium acetate **3** using 10 mol % NH_4VO_3 as a catalyst in different solvents. From Table 1, we observed reaction in DMF and water at 90°C afforded the product in low yields even after heating for 10 and 12 h, respectively (Table 1, entries 1 and 3). The use of THF at reflux temperature does not proceed the reaction (Table 1, entry 2), but we have observed that the reaction gives 90% yield in DMSO at 90°C and 91% yield in absolute ethanol at reflux temperature (Table 1, entries 4 and 6). The reaction also carried out in methanol at reflux temperature, and the yield was good (90%) but requires more time (Table 1, entry 5). We have performed the above model reaction by combination of ethanol and water as a co-solvent system, but absolute ethanol was observed better solvent for this reaction (Table 2). It was also observed that among the tested solvents (Table 2, entries 1), the reaction in absolute alcohol was more facile in terms of time and yield.

By keeping absolute ethanol as a solvent for model reaction, the concentration of ammonium metavanadate also been studied. At 5, 7.5, 10, and 12.5 mol % of ammonium metavanadate gives the corresponding triaryl imidazole in 68, 87, 91, and 91%, respectively, are shown in Table 3.

We have carried out the same cyclocondensation reaction with various aromatic/heteroaromatic aldehydes containing electron-donating or -withdrawing functional groups at different positions worked well and did not show remarkable differences in the yields of product and reaction time, and the results are shown in Table 4. Under similar reaction conditions, we have carried out the cyclocondensation of benzoin **1b** with aromatic/heteroaromatic aldehydes and ammonium acetate in the presence of ammonium metavanadate that resulted into the corresponding triaryl imidazoles in good yields. However, the reaction requires more time when compared with benzil (Table 4). The formation of triaryl imidazoles have been confirmed by physical and spectroscopic data and is in full agreement with reported data. Also, the present method was found to be effective for benzil compared with benzoin in terms of time and yield.

The present study was then extended for the synthesis of 1,2,4,5-tetraaryl-1*H* imidazoles via the one-pot, four-component condensation of benzil (**1a**), aldehydes **2**, ammonium acetate **3**, and aromatic primary amines **4**. To our delight, the 1,2,4,5-tetraaryl-1*H*-imidazoles were obtained in high yields. The results were illustrated in (Table 4, entries 4j and 4k).

The role of NH_4VO_3 has been proposed to activate the aldehyde by binding the oxygen atom of aldehyde with vacant ''d'' orbital of transition metal vanadium to achieve the stable oxidation state. Along with this, we recovered the catalyst and reused for further reactions. The catalyst was recovered by filtration and washed with diethyl ether and dried at 60–70°C, which was then dissolved in dilute sulphuric acid to transform it from (V) to (IV) oxidation state. A little bit of zinc powder was then added with constant swirling and warming to reduced V (V) to vanadium compounds with lower oxidation state (IV), as evident by the color of the solution changes to Persian blue reported in the literature [33].

Table 1

Screening of solvents.[a]

Entry	Solvent	Time	Yield (%)[b]
1	DMF	10 (h)	75
2	THF	12 (h)	No reaction
3	H_2O	12 (h)	30
4	DMSO	1 (h)	90
5	MeOH	2 (h)	90
6	EtOH	45 (min)	91

[a] Reaction conditions: **2a** (1 mmol), **1** (1 mmol), NH_4VO_3 (10 mol %), solvent (10 mL).
[b] Isolated yields.

Table 2

Solvent effect for model reaction **4a**.

Entry	Solvent	Time	Yield (%)[a]
1	EtOH (100%)	45 (min)	91
2	EtOH + H_2O (50:50)	1.3 (h)	89
3	EtOH + H_2O (20:80)	2 (h)	85
4	EtOH + H_2O (10:90)	2.3 (h)	80

[a] Isolated yields.

Table 3

Effect of catalyst concentration on model reaction **4a**.

Entry	Catalyst (mol %)	Yield (%)[a]
1	5	68
2	7.5	87
3	10	91
4	12.5	91

[a] Isolated yield.

EXPERIMENTAL

All the melting points were determined in open capillaries in a paraffin bath and are uncorrected. ^{1}H-NMR spectra were recorded on Mercury Plus Varian in DMSO or $CDCl_3$ at 400 MHz using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR using KBr discs. Mass spectra were recorded on Micromass Quattro II using electrospray ionization technique. The elemental analysis was carried out on Flash EA 1112, 50/60 Hz, 1400 VA CHNS analyzer. The progress of the reactions was monitored by TLC.

General procedure for the synthesis of 2,4,5-triaryl-1H-imidazoles (4a–i). To the stirred mixture of aldehyde **2** (1 mmol), benzil **1a** or benzion **1b**, (1 mmol), and ammonium acetate **3** (1.5 mmol) in ethanol (10 mL), ammonium metavanadate (10 mol %) was added. The reaction mixture was refluxed as time indicated in Table 4.

The progress of the reaction was monitored by TLC (ethyl acetate: hexane, 7:3). After completion of reaction, dichloromethane (25 mL) was added to the reaction mixture, and it was then washed with water (10 mL) and dried over anhydrous $CaCl_2$, and the solvent evaporated in vacuum to give the crude product. Purification of solid products was achieved by crystallization from EtOH. Products are known compounds and were characterized by comparison of their spectral data (IR, mass, and ^{1}H-NMR) and physical properties with those reported in the literature.

2,4,5-Triphenyl-1H-imidazole (4a). M.p.: 275–277°C (lit [25] 276–278°C). IR (KBr, cm^{-1}): 7125, 3040, 1485, 1459, 1130, 695. ^{1}H-NMR (400 MHz, DMSO-d_6, δ ppm): 12.72 (brs, 1H, NH), 8.12 (d, 2H, J = 7.6 Hz, ArH), 7.40–7.52 (m, 13H, ArH). MS (EI): m/z (%) = 296 (46) [M$^+$]. Anal. calcd. for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.07; H, 5.41; N, 9.52.

2-(4-Chlorophenyl)-4,5-diphenyl-1H-imidazole (4b). M.p.: 261–263°C (lit [25] 260–262°C). IR (KBr, cm^{-1}): 3062, 1606, 1453, 1090, 763, 695. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm): 12.80 (brs, 1H, NH), 8.10 (d, 2H, J = 8.4 Hz, ArH), 7.22–7.58 (m, 12H, ArH). MS (EI): m/z (%) = 330 (36), 332 (12) [M$^+$]. Anal. calcd. for $C_{21}H_{15}C_lN_2$: C, 76.24; H, 4.57; N, 8.47. Found: C, 76.20; H, 4.55; N, 8.51.

2-(2-Chlorophenyl)-4,5-diphenyl-1H-imidazole (4c). M.p.: 194–196°C (lit [25] 195–196°C). IR (KBr, cm^{-1}): 3432, 3066, 1630, 1506, 1499. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm): 12.48 (brs, 1H, NH), 7.25–7.59 (m, 14H, ArH). MS (EI): m/z (%) = 330 (36), 332 (12) [M$^+$]. Anal. calcd. for $C_{21}H_{15}C_lN_2$: C, 76.24; H, 4.57; N, 8.47. Found: C, 76.20; H, 4.55; N, 8.51.

2-(4-Methoxyphenyl)-4,5-diphenyl-1H-imidazole (4d). M.p.: 227–229°C (lit [25] 227–228°C). IR (KBr, cm^{-1}): 3030, 1612, 1492, 1250, 1032, 695. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm): 12.53 (brs, 1H, NH), 8.02 (d, 2H, J = 8.0 Hz, ArH), 7.52 (d, 4H, J = 6.8 Hz, ArH), 7.30–7.37 (m, 6H, ArH), 7.05 (d, 2H, J = 7.6 Hz, ArH), 3.82 (s, 3H, CH_3). MS (EI): m/z (%) = 326 (36) [M$^+$]. Anal. calcd. for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 80.94; H, 5.53; N, 8.63.

2-(2-Nitrophenyl)-4,5-diphenyl-1H-imidazole (4e). M.p.: 230–232°C (lit [25] 232–233°C). IR (KBr, cm^{-1}): 3422, 3088, 1590, 1505, 1336, 1105. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm) 12.65 (s, NH), 8.03 (d, ^3J = 7.5 Hz, $C_6H_4NO_2$), 7.08–7.60 (m,

Table 4

Synthesis of 2,4,5-triaryl-1*H*-imidazoles **4(a–i)** using. NH_4VO_3 as a catalyst.[a]

Entry	Compounds	R	1	Time (min)	Yield (%)[c]	Melting point (°C)	
						Found	Reported
1	**4a**	H	Benzil	45	94	275–277	276–278 [25]
2	**4b**	4-Cl	Benzil	60	92	261–263	260–262 [25]
3	**4c**	2-Cl	Benzil	50	90	194–196	195–196 [25]
2	**4d**	4-OMe	Benzil	55	94	227–229	227–228 [25]
5	**4e**	4-NO_2	Benzil	60	89	230–232	232–233 [25]
6	**4f**	4-F	Benzil	55	94	188–189	190 [25]
7	**4g**	2-Thienyl	Benzil	45	89	261–262	260–261 [25]
8	**4h**	2-Furyl	Benzil	60	92	198–200	199–201 [25]
9	**4i**	4-OH	Benzil	65	88	270–272	268–270 [25]
10	**4j**[b]	4-OMe	Benzil	120	82	175–178	174–175 [23]
11	**4k**[b]	4-OH	Benzil	150	80	283–285	287–289 [23]
12	**4a**	H	Benzoin	100	90	–	–
13	**4b**	4-Cl	Benzoin	90	89	–	–
14	**4h**	2-Furyl	Benzoin	90	87	–	–
15	**4d**	4-OMe	Benzoin	85	88	–	–
16	**4g**	2-Thienyl	Benzoin	120	85	–	–

[a] Reaction conditions: benzil/benzoin (1 mmol), aldehyde (1 mmol), ammonium acetate (1.5 mmol), NH_4VO_3 (10 mol %).
[b] Reaction conditions: benzil(1 mmol), aldehyde (1 mmol), aromatic primary amines (1 mmol), ammonium acetate (1.5 mmol), NH_4VO_3 (10 mol %).
[c] Isolated yields.

$2C_6H_5$), 6.69 (d, $^3J = 7.4$ Hz, $C_6H_4NO_2$). MS (EI): *m/z* (%) = 297 (60), 269 (20), 165 (100), 105 (25), 77 (50). Anal. calcd. for $C_{21}H_{15}N_3O_2$: C, 73.90; H, 4.39; N, 12.31. Found: C, 73.83; H, 4.32; N, 12.39.

2-(2-Fluorophenyl)-4,5-diphenyl-1H-imidazole (4f). M.p.: 188–189°C (lit [25] 190°C). IR (KBr, cm^{-1}): 3027, 1495, 1234, 837, 765, 695. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm): 12.71 (brs, 1H, NH), 8.13 (d, 2H, J = 4.2 Hz, ArH), 7.57 (d, 4H, J = 5.6 Hz, ArH), 7.25–7.40 (m, 8H, ArH). MS (EI): *m/z* (%) = 314 (44) [M^+]. Anal. calcd. for $C_{21}H_{15}FN_2$: C, 80.24; H, 4.81; N, 8.91. Found: C, 80.27; H, 4.79; N, 8.86.

2-(2-Furyl)-4,5-diphenyl-1H-imidazole (4h). M.p.: 198–200°C (lit [25] 199–201°C). IR (KBr, cm^{-1}): 3318, 2989, 2470, 1660, 1212, 1170, 874, 717, 637. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm): 7.95–8.02 (m, 6H, Ar), 7.60–7.70 (m, 3H, Ar), 7.46–7.58 (m, 4H, Ar), 7.20 (m, 1H, NH). MS (EI) (*m/z*, %) = 286 (29) [M^+]. Anal. calcd. for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N,9.78. Found: C, 79.66; H, 4.91; N, 9.74.

2-(2-Hydroxyphenyl)-4,5-diphenyl-1H-imidazole (4i). M.p.: 270–272°C (lit [25] 268–270°C). IR (KBr, cm^{-1}): 3283, 3057, 1702, 1608, 1493, 696. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm): 12.42 (s, 1H, NH), 9.71 (s, 1H, OH), 7.90 (d, 2H, J = 8.4 Hz, ArH), 7.54 (d, 2H, J = 7.6 Hz, ArH), 7.49 (d, 2H, J = 7.2 Hz, ArH), 7.42 (t, 2H, J = 7.6 Hz, ArH), 7.35 (t, 1H, J = 7.6 Hz, ArH), 7.29 (t, 2H, J = 7.6 Hz, ArH), 7.21 (t, 1H, J = 7.2 Hz, ArH), 6.85 (d, 2H, J = 8.4 Hz, ArH). MS (EI): *m/z* (%) = 312 (40) [M^+]. Anal. calcd. for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.70; H, 5.18; N, 8.93.

2-(4-Methoxyphenyl)-1,4,5-triphenyl-1H-imidazole (4j). M.p.: 175–178°C (lit [23] 174–175°C) IR (KBr, cm^{-1}): 3061, 2954, 1605, 1570, 1481. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm): 7.62 (d, 2H, J = 8.0 Hz, ArH), 7.01–7.37 (m, 15H, ArH), 6.77 (d, 2H, J = 8.0 Hz, ArH), 3.77 (s, 3H, OCH_3). MS (EI): *m/z* (%) = 403 [M^+]. Anal. calcd. for $C_{28}H_{22}N_2O$: C, 83.56; H, 5.51; N, 6.96. Found: C, 83.57; H, 5.53; N, 6.95.

4-(1,4,5-Triphenyl-1H-imidazol-2-yl)phenol (4k). M.p.: 283–285°C (lit [23] 287–289°C) IR (KBr, cm^{-1}): 3430, 3057, 1610, 1581, 1499. ^{1}H-NMR (400 MHz, DMSO-d_6 δ ppm): 9.30 (s, 1H, OH), 7.58–7.62 (d, 2H, J = 8.1 Hz, ArH), 7.15–7.53 (m, 15H, ArH), 6.74 (d, 2H, J = 8.0 Hz, ArH). MS (EI): *m/z* (%) = 389 [M^+]. Anal. calcd. for $C_{27}H_{20}N_2O$: C, 83.48; H, 5.19; N, 7.21. Found: C, 83.50; H, 5.21; N, 7.25.

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