Phosphomolybdic acid Catalyzed Facile One-pot Synthesis of 2,4,5-Triaryl-1*H*-imidazoles From Benzil and Aromatic Aldehydes

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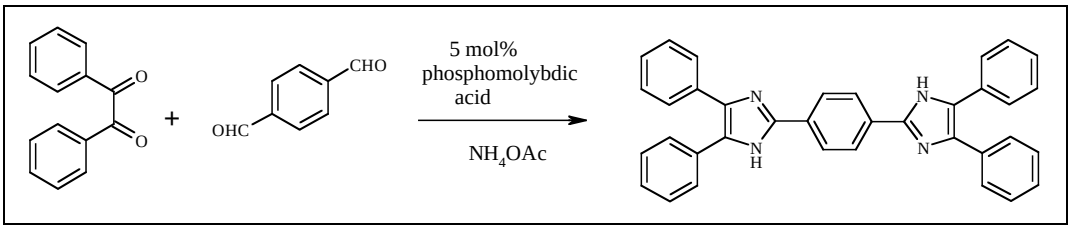

A facile one-pot synthesis of 2,4,5-triaryl-1*H*-imidazoles with better yields and shorter reaction time from the condensation of benzil, ammonium acetate and aromatic aldehydes using the catalyst phosphomolybdic acid is described

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INTRODUCTION

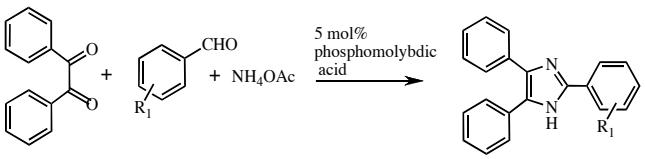
Substituted imidazoles are one of the most important heterocyclic compounds found in a large number of natural products and pharmacologically active compounds like the amino acid histidine, the hypnotic agent etomidate, [1] the antiulcerative agent cimetidine, [2] the proton pump inhibitor omeprazole, [3] the fungicide ketoconazole, [4] and the benzodiazepine antagonist flumazenil [5]. Also, the substituted imidazoles are substantially used in ionic liquids, [6] that have been given a new approach to 'Green Chemistry'. In addition, they are used in photography as photosensitive compound [7]. There are several methods in the literature for synthesis of these compounds, mainly using nitriles and esters [8] as the starting substrates. Japp and Radziszewski proposed the first synthesis of the imidazole core in 1882, starting from 1,2-dicarbonyl compounds aldehydes and ammonia, to obtain 2,4,5-triphenyl-1*H*-imidazoles. [9] Subsequently, many other syntheses of this important heterocycle have been published [10]. For example, 2,4-diaryl-1*H*-imidazoles are often obtained from amidines and α-bromo arylketones [11]. Moreover, Zhang and Chen described an efficient procedure to obtain unsymmetrical, C5 unsubstituted 2,4-diarylimid-azoles. In this approach acetophenones are oxidized *in situ* to α-tosyloxyacetophenones, which then are condense with arylamidines to obtain the desired compounds [12]. However, some of theses previous methods have suffered from one or more drawbacks like high temperature requirement, highly acidic conditions, and the use of metal cyanides for preparation of the nitrile compounds that limit their uses [13]. Some of methods require harsh conditions [14]. Therefore, the development of a mild, efficient and versatile method is still strongly desirable. Herein, we have presented a novel, mild and efficient method for synthesis of 2,4,5-triarylimidazole using phosphomolybdic acid ($H_3PO_4.12MoO_3.24H_2O$) catalyst. The use of phosphomolybdic acid as a catalyst is increasing due to its mild acidic character. It is widely used for the bulk polymerization of styrenes and the catalytic and selective deprotection of *tert*-butyldimethyl-silyl ether [15]. In the present article, we have used phosphomolybdic acid catalyst to develop a simple and facile synthetic method for preparation of triarylimidaz-oles using benzil, ammonium acetate and aromatic alde-hydes.

RESULTS AND DISCUSSION

The reaction conditions were standardized for the representative example of the preparation of 2,4,5-triphenyl-1*H*-imidazole (**3**) from benzil, ammonium acetate and benzaldehyde (Scheme – 1) in different solvents and various mol% of phosphomolybdic acid catalyst (Table - 1).

Scheme 1

Synthesis of 2,4,5-triarylimidazoles using benzil, aromatic aldehydes, ammonium acetate and 5 mol% phosphomolybdic acid catalyst.



1 **2** **3**

From the results obtained, the optimized reaction conditions were use of acetonitrile-water (1:1) solvent system and 5 mol% of phosphomolybdic acid catalyst at heating (80 °C).

Table 1

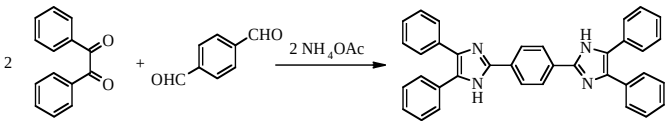
Optimization of reaction conditions for synthesis of 2,4,5-triaryl-1*H*-imidazoles using 5 mol% phosphomolybdic acid catalyst.

Solvent	Reaction time (min)	Yield (%)
Acetonitrile	50	86
THF	55	81
DMF	50	78
THF-water (1:1)	45	92
Acetonitrile - water (1:1)	40	98

Using the optimized reaction conditions, a range of 2-aryl-4,5-diphenyl-1*H*-imidazoles were synthesized and the results are summarized in Table 2. From the results obtained, the aromatic aldehydes with elctron-donationg substituents (**3a**, and **3b**) favor the reaction and reaction times are shorter reaction than for the aldehydes with electron withdrawing substituents (**3f**). For the *p*-nitro-benzaldehyde (**3f**), the reaction was very slow and also it was a low yielding reaction. The method was also found to be effective for hetero-aromatic aldehydes for the synthesis 2-heteroaryl-4,5-diphenylimidazoles with higher yields (**3i**, **3j**, and **3k**). The present method was superior to the available methods with regards to yields and reaction time [16]. Especially for the preparation of 2-(4-methylphenyl)-4,5-diphenyl-1*H*-imidazole (**3b**) which was synthesized in 96% yield while the reported yield was 74 % and also 2-(2-chlorophenyl)-4,5-diphenyl-1*H*-imid-azol (**3e**) was synthesized in 94% while the reported yield was 85 % [17].

Scheme 2

Synthesis bis-(2,4,5-triaryl-1*H*-imidazoles) using benzil, ammonium acetate, benzene-1,4-dicarboxaldehyde and 5 mol% phosphomolybdic acid



The methodology was also extended for the synthesis of bis-imidazoles like 4,5-diphenyl-2-(4-(4,5-diphenyl-1*H*-imidazol-2-yl)phenyl)-1*H*-imidazole (Scheme 2) using two equivalents of substituted benzil, ammonium acetate and the benzene-1,4-dicarboxaldehyde. The results obtained were summarized in table 3. The method was found to be efficient and yields obtained were in the range of 87% to 96%. All the synthesized compounds were characterized with mass, and ^{1}H NMR and found to be matching with the corresponding compounds.

Table 3

Synthesis bis-2,4,5-triaryl-1*H*-imidazoles using benzil, ammonium acetate, benzene-1,4-dicarboxaldehyde and 5 mol% phosphomolybdic acid.

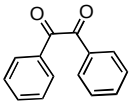
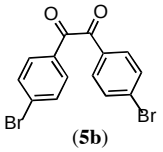
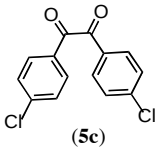
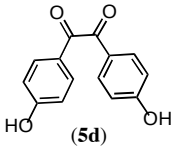
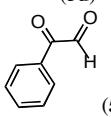
Entry	Benzil	Reaction Time (min)	Yield (%)
1	 (**5a**)	55	93
2	 (**5b**)	50	81
3	 (**5c**)	60	94
4	 (**5d**)	50	91
5	 (**5e**)	50	92

Table 2

Synthesis 2,4,5-triaryl-1*H*-imidazoles using benzil, ammonium acetate, aromatic aldehydes, and 5 mol% phosphomolybdic acid.

Entry No.	Ar-CHO	Compound No.	Reaction time (min)	Yield (%)	Melting points	
					Found	Lit.[17,18,19]
1	Ph-	**3a**	45	97	275 - 277	275-276[17]
2	4-Me-Ph-	**3b**	40	96	230 - 231	230-231[17]
3	4-OMe-Ph-	**3c**	45	94	226 - 227	226-228[17]
4	4-OH-Ph-	**3d**	50	95	268 - 269	267-268[17]
5	2-Cl-Ph-	**3e**	50	95	196 - 197	196-197[17]
6	4-NO_2-Ph-	**3f**	70	87	235 - 237	238-239[17]
7	4-Cl-Ph-	**3g**	60	93	258 - 261	261-262[17]
8	4-$(CH_3)_2$N-Ph-	**3h**	55	92	255 - 257	256-258[17]
9	2-thionyl-	**3i**	65	89	253 -255	254-255[18]
10	4-Pyridyl-	**3j**	50	92	234 - 236	235-236[19]
11	2-Furyl-	**3k**	50	95	199 - 202	202-203[17]

The use of the cheap and easily available phosphomolybdic acid as a catalyst is an advantageous aspect of the present method. Since, the reaction protocol and work-up used is simple and practical, the methodology could be useful for multi-scale reactions. Water was utilized in reaction as solvent and for work-up also. Therefore, the presented method was also supporting to the Green Chemistry.

In conclusion, using 5 mol% phosphomolybdic acid catalyst, 2,4,5-triaryl-1*H*-imidazoles were efficiently synthesized with moderate to excellent yields from benzil, ammonium acetate and aromatic aldehydes. Also the method was efficiently used for the synthesis of bis-substituted imidazoles from substituted benzil substrates, ammonium acetate and 1,4-phenyl dicarboxaldehyde. The advantages of the reported method are the use of cheap and easily available catalyst, shorter reaction time and better yields.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a 400 MHz Varian-Gemini spectrometer and are reported as parts per million (ppm) downfield from a tetramethylsilane internal standard. The following abbreviations are used; singlet (s), doublet (d), triplet (t), quartet (q), multiplate (m) and broad (br). Mass spectra were taken with Micromass - QUATTRO-II of WATER mass spectrometer. HPLC was performed using Zorbax SB-C18 reverse phase column (0.46 X 25 cm) on Shimadzu instrument equipped with an automatic injector with UV-PDA detector. Detection was carried out at 254 nm. The mobile phase consists of 0.05 % TFA and acetonitrile (1:1, V/V). The products were eluted at flow rate of 1 mL/min using isocratic method. Flash column chromatography was performed with 300-400 mesh silica gel and analytical thin layer chromatography was performed on precoated silica gel plates (60F-254) with system (v/v) indicated. Melting points were determined in capillary tubes and are uncorrected.

General method for the synthesis of 2,4,5-triaryl-1*H*-imidazoles. A mixture of phosphomolybdic acid (5 mol%), ammonium acetate (30 mmol), and benzil (10 mmol) was dissolved in acetonitrile-water (20 mL, 1:1, v/v). To the reaction mixture, aromatic aldehyde (12 mmol) was added and was heated at 80 °C untill the reaction is complete (TLC). The reaction mixture was then cooled to room temperature and poured on ice-water (50 mL) to obtain the solid precipitated. The solid was collected by filtration, washed with water and dried to give the corresponding 2,4,5-triaryl-1*H*-imidazoles.

All synthesized compounds were characterized with ^{1}H NMR and mass. Also the melting points were recorded and compared with those of corresponding literature melting points and found to be in agreement with literature values. The representative analytical data are given below:

2,4,5-Triphenyl-1*H*-imidazole (3a). Off-white solid, HPLC purity - 98 %; ^{1}H NMR (400 MHz, DMSO): δ = 7.55 - 7.68 (m, 6H), 7.72 – 7.75 (m, 3H), 7.9 - 7.95 (m, 6H), 8.8 (bs, 1H); MS (EI, 70 eV): *m/z* = 297 $[M+H]^+$; Anal Calc. $C_{21}H_{16}N_2$ (296): calcd C, 85.11, H, 5.44, N, 9.45; found C, 85.18, H, 5.33, N, 9.47.

2-(4-Methylphenyl)-4,5-diphenyl-1*H*-imidazole (3b). Off-white solid, HPLC purity - 99%; ^{1}H NMR (400 MHz, DMSO): δ = 2.25 (s, 3H), 6.72–6.75 (d, J=8.6 Hz, 2H), 7.25 –7.55 (m, 10H), 8.0 (d, J=8.6 Hz, 2H), 12.0 (brs, 1H); MS (EI, 70 eV): *m/z* = 310 $[M+H]^+$; $C_{22}H_{18}N_2$ (310): calcd C, 85.13, H, 5.85, N, 9.02; found C, 85.19, H, 5.88, N, 8.98.

2-(4-Methoxy-phenyl)-4,5-diphenyl-1*H*-imidazole (3c). Off-white solid, HPLC purity - 97 %; ^{1}H NMR (400 MHz, DMSO): δ = 3.85 (s, 3H), 6.93–6.96 (d, J=8.4 Hz, 2H), 7.25 – 7.59 (m, 10H), 8.02–8.05 (d, J=8.4 Hz, 2H), 12.52 (brs, 1H); MS (EI, 70 eV): *m/z* = 327 $[M+H]^+$; $C_{22}H_{18}N_2O$ (326): calcd C, 80.96, H, 5.56, N, 8.58; found C, 81.13, H, 5.52, N, 8.60.

2-(4-Hydroxyphenyl)-4,5-diphenyl-1*H*-imidazole (3d). Off-white solid, HPLC purity - 96 %; ^{1}H NMR (400 MHz, DMSO): δ =5.2 (bs, 1H), 6.93-6.97(d, J=8 Hz, 2H), 7.52-7.87(m, 10H), 7.88-7.92 (d, J= 8.5Hz, 2H), 12.58 (brs, 1H); MS (EI, 70 eV): *m/z* = 312 $[M+H]^+$; $C_{21}H_{16}N_2O$ (312): calcd C, 80.75, H, 5.16, N, 8.97; found C, 80.68, H, 5.05, N, 8.90.

2-(2-Chorophenyl)-4,5-diphenyl-1*H*-imidazole (3e). Off-white solid, HPLC purity - 97 %; ^{1}H NMR (400 MHz, DMSO): δ = 7.27-7.37(m, 10H), 7.45-7.49 (dd, J = 9 Hz, 1H), 7.57-7.59 (d, J = 8 Hz, 2H), 8.02-8.05 (dd, J =8.79 Hz, 1H), 12.5(brs, 1H); MS (EI, 70 eV): *m/z* = 330 $[M+H]^+$; $C_{21}H_{15}ClN_2$: calcd C, 76.24, H, 4.57, N, 8.47; found C, 76.12, H, 4.49, N, 8.38.

2-(4-Nitro-phenyl)-4,5-diphenyl-1*H*-imidazole (3f). Off-white solid, HPLC purity - 98 %; ^{1}H NMR (400 MHz, DMSO): δ = 7.3 –7.57 (m, 10H), 7.78 (d, 2H), 8.3 (d, 2H), 12.6 (brs, 1H); MS (EI, 70 eV): *m/z* = 342 $[M+H]^+$, $C_{21}H_{15}N_3O_2$: calcd C, 73.89, H, 4.43, N, 12.31; found C, 73.83, H, 4.39, N, 12.36.

2-(4-Chorophenyl)-4,5-diphenyl-1*H*-imidazole (3g). Off-white solid, HPLC purity - 98 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.5 - 7.65 (m, 6H), 7.68 – 7.72 (m, 2H), 7.9 – 8.0 (m, 6H), 8.7 (bs, 1H); MS (EI, 70 eV): *m/z* = 330 $[M+H]^+$; $C_{21}H_{15}ClN_2$: calcd C, 76.24, H, 4.57, N, 8.47; found C, 76.27, H, 4.59, N, 8.45.

2-(4-*N*,*N*-Dimethyl)-4,5-diphenyl-1*H*-imidazole (3h). Off-white solid, HPLC purity - 99 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.9 (s, 6H), 7.1 (d, *J* = 8.2 Hz, 2H), 7.4 - 7.55(m, 4H), 7.65 – 7.7 (m, 2H), 7.8 - 7.95 (m, 6H), 8.7 (bs, 1H); MS (EI, 70 eV): *m/z* = 339 $[M+H]^+$; $C_{23}H_{21}N_3$: calcd C, 81.39, H, 6.24, N, 12.38; found C, 81.42, H, 6.23, N, 12.34.

2-(4-Pyridyl)-4,5-diphenyl-1H-imidazole (3i). Off-white solid, HPLC purity - 98 %; mp 256-258, ^{1}H NMR (400 MHz, DMSO): δ = 7.27-7.37(m,10H), 7.6-7.65 (d, J= 8.6Hz, 2H), 8.7 – 8.75 (d, J=8.6 Hz, 2H), 12.45(brs, 1H); MS (EI, 70 eV): *m/z* = 297 $[M+H]^+$; $C_{20}H_{15}N_3$: calcd C, 80.78, H, 5.08, N, 14.13; found C, 80.81, H, 5.05, N, 14.12.

2-(2-Thionyl)-4,5-diphenyl-1*H*-imidazole (3j). Off-white solid, HPLC purity - 98 %; ^{1}H NMR (400 MHz, DMSO): δ = 6.8 (d, J=8.4 Hz, 1H), 7.1 (dd, J=8.4 and 8.1 Hz, 1H), 7.25-7.35(m, 11H), 12.2 (brs, 1H); MS (EI, 70 eV): *m/z* = 302 $[M+H]^+$; $C_{19}H_{14}N_{2S}$: calcd C, 75.47, H, 4.67, N, 9.26; found C, 75.44, H, 4.70, N, 9.26.

2-(2-Furylphenyl)-4,5-diphenyl-1*H*-imidazole (3k). Off-white solid, HPLC purity - 97 %; ^{1}H NMR (400 MHz, DMSO): δ = 6.7(d, J =7.8 Hz, 1H), 7.1 (dd, J = 7.8 Hz, 1H), 7.25-7.35(m, 11H), 11.8 (bs, 1H); MS (EI, 70 eV): *m/z* = 287 $[M+H]^+$; $C_{19}H_{14}N_2O$: calcd C, 79.72, H, 5.24, N, 9.79; found C, 79.31, H, 5.21, N, 9.74.

General method for the synthesis of bis-(2,4,5-substituted-1*H*-imidazoles). A mixture of phosphomolybdic acid (5 mol%), ammonium acetate (60 mmol), and benzil (22 mmol) was dissolved in acetonitrile-water (30 mL, 1:1, v/v). To the reaction

mixture, 1.4-phenyl-dicarboxaldehyde (10 mmol) was added and was heated at 80 °C until the reaction is complete (TLC). The reaction mixture was cooled to room temperature and poured on ice-water (70 mL). It was extracted with ethyl acetate twice and collectively the organic layer washed with brine, dried over sodium sulphate and purified with silica gel column chromatography to give the corresponding products. The representative analytical data for

4,5-Diphenyl-2-(4-(4,5-diphenyl-1*H*-imidazol-2-yl)phenyl)-1*H*-imidazole (5a). Off-white solid, HPLC purity - 99%, mp 232-233, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.3-7.45 (m, 10H), 7.65 - 7.7 (m, 4H), 7.9-8.0 (m, 10H), 12.25 (bs, 2H); MS (EI, 70 eV): *m/z* = 515 $[M+H]^+$; $C_{36}H_{26}N_4$: calcd C, 84.02, H, 5.09, N, 10.89; found C, 83.98, H, 5.11, N, 10.87.

4,5-Di-(4-bromophenyl)-2-(4-(4,5-di(4-bromophenyl)-1*H*-imidazol-2-yl)phenyl)-1*H*-imidazole (5b). Off-white solid, HPLC purity - 97%, mp 211-213, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.40 (m, 8H), 7.52 - 7.55 (m, 4H), 8.0-8.2 (m, 8H), 12.20 (bs, 2H); MS (EI, 70 eV): *m/z* = 831 $[M+H]^+$; $C_{36}H_{22}Br_4N_4$: calcd C, 52.08, H, 2.67, N, 6.75; found C, 52.14, H, 2.64, N, 6.71.

4,5-Di-(4-chlorophenyl)-2-(4-(4,5-di(4-bromophenyl)-1*H*-imidazol-2-yl)phenyl)-1*H*-imidazole (5c). Off-white solid, HPLC purity - 98%, mp 249-251, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.34 (m, 8H), 7.45 - 7.50 (m, 4H), 7.78 -7.95 (m, 8H), 12.20 (bs, 2H); MS (EI, 70 eV): *m/z* = 653 $[M+H]^+$; $C_{36}H_{22}Cl_4N_4$: calcd C, 66.28, H, 3.40, N, 8.59; found C, 66.29, H, 3.38, N, 8.63.

4,5-Di-(4-phenoxyl)-2-(4-(4,5-di(4-phenoxyl)-1*H*-imidazol-2-yl)phenyl)-1*H*-imidazole (5d). Off-white solid, HPLC purity - 97%, mp 263-265, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.9(bs, 2H), 6.8-6,85(m, 8H), 7.35 - 7.4(m, 4H), 7.62-7.8 (m, 8H), 11.6(bs, 2H); MS (EI, 70 eV): *m/z* = 578 $[M+H]^+$; $C_{36}H_{26}N_4O_4$: calcd C, 74.73, H, 4.53, N, 9.68; found C, 73.96, H, 4.58, N, 9.66.

5-Phenyl-2-(4-(5-phenyl-1*H*-imidazol-2-yl)phenyl)-1*H*-imidazole (5e). Off-white solid, HPLC purity - 98%, mp 187-289, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.8(s, 2H), 7.2 - 7.32(m, 6H), 7.45 - 7.48(m, 4H), 7.62-7.65 (m, 4H), 12.9(bs, 2H); MS (EI, 70 eV): *m/z* = 363 $[M+H]^+$; $C_{24}H_{18}N_4$: calcd C, 79.54, H, 5.01, N, 15.46; found C, 79.59, H, 4.96, N, 15.41.

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