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Synthesis and Luminescence-Structure Relationship of 2,4,5-Triarylimidazoles

SHU-NING YUE[1], YU WAN[2], LING YE[1], WEN-LI ZHANG[1], HAO CUI[1], LI-ZHUO ZHANG[1], QIU-JU ZHOU[1], HUAN ZOU[1], ZHEN-TAO LIU[1], LING-LING ZHAO[1], SHENG-LIANG ZHOU[2] and HUI WU[1,2,*]

[1]School of Chemistry and Chemical Engineering, Jiangsu Normal University, Jiangsu Key Laboratory of Green Synthesis of Functional Material, Xuzhou 221116, P.R. China
[2]Jiangsu Key Laboratory of Biotechnology on Medical Plant, Xuzhou 221116, P.R. China

*Corresponding author: Fax: +86 516 83500164; Tel: +86 516 83403163; E-mail: wuhui72@126.com

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2,4,5-Triarylimidazoles were efficiently synthesized with excellent yields (90-96 %) *via* the one-pot concentration of benzil, aromatic aldehyde and ammonium acetate in ionic liquid [BMIM][BF_4] in the present of acetic acid. The luminescence-structure relationship of products was investigated.

Keywords: Synthesis, Luminescence-structure relationship, 2,4,5-Triarylimidazoles.

INTRODUCTION

The imidazole core is a fertile source of biologically important molecules. Compounds containing imidazole moiety have many pharmacological properties and play important roles in biochemical processes. They act as potent and selective inhibitors of p38 MAP kinase[1], B-Raf kinase[2], cyclooxygenase-2 (COX-2)[3] and biosynthesis of interleukin-1 (IL-1)[4]. Many of the substituted imidazoles are known as antibacterial[5], antitumor agents[6] and also as pesticides[7]. In addition, 2,4,5-triaryl substituted imidazoles possess non-coplanar structure, which is beneficial to retard aggregation[8]. So the arylated imidazoles not only show the above-mentioned traits but also act as an emitting chromophore in a molecular design which will be beneficial for favorable properties such as emission color purity, photoluminescence quantum yield and thermal stability[9].

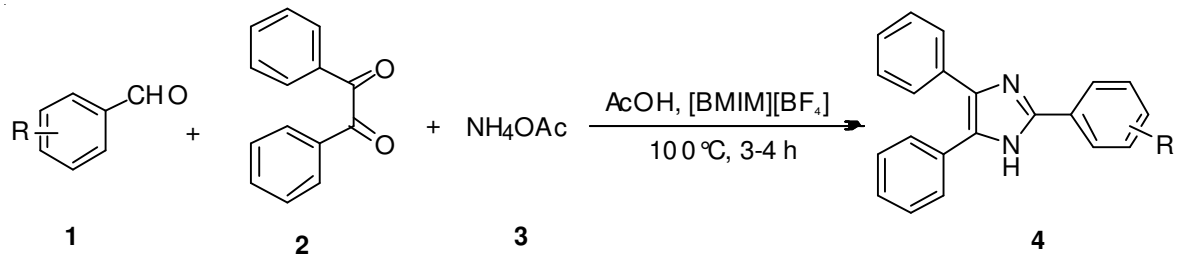
Therefore, numerous methods have been flourished for the preparation of 2,4,5-trisubstituted imidazoles such as the hetero-cope rearrangement[10], four-component condensation of arylglyoxals, primary amines, carboxylic acids and isocyanides on Wang resin[11]. Recently, the synthesis of 2,4,5-trisubstituted imidazoles has been catalyzed by $ZrCl_4$[12], ionic liquid[13], silica gel or Zeolite HY[14] and also by microwave irradiation using acetic acid as promotor. However, most of these methods suffered from one or more drawbacks, such as complex work-up and purification, significant amounts of waste materials, occurrence of side reactions, low yields and the use of expensive reagents. Additionally, many of them required elevated temperatures created by microwave irradiation at 180-200 °C. Therefore, the development of a mild and efficient way for synthesis of this valuable heterocycle to overcome previous shortcomings is still a serious challenge.

Recently, ionic liquids (ILs) have attracted much attention as promising alternative 'green' solvents to hazardous traditional organic solvents, due to their properties such as non-flammability, negligible vapour pressure, high thermal stability, solvating ability and easy recyclability[15]. We now report a simple, environment-friendly and efficient method one-pot synthesis of 2,4,5-triarylimidazoles in excellent yields in ionic liquid [BMIM][BF_4] in the present of acetic acid. The luminescence-structure relationship of products was investigated in detail *via* ultraviolet absorption and fluorescence spectra.

EXPERIMENTAL

All melting points are uncorrected and were measured on XT5 melting point apparatus. The NMR spectra were run on a Bruker Avance DMX 400 spectrometer in DMSO-d_6 using TMS as internal standard. Fluorescence spectrum was reported on F-4500 Fluorescence Spectrophotometer (Hitachi, Japan). The IR spectra were obtained in potassium bromide pellets with a Bruker 27FTIR-Tensor using KBr optics. The ultraviolet absorption spectrum was measured with a Tu-1201 ultraviolet spectrophotometer (Shimadzu). All reagents were obtained from commercial suppliers and used without further purification.

Synthesis of 2,4,5-triarylimidazoles (Scheme-I): The mixture of aromatic aldehyde **1** (1 mmol), benzil **2** (1 mmol),



Scheme-I: Synthesis of 2,4,5-triarylimidazoles

ammonium acetate (NH_4OAc) **3** (5 mmol), acetic acid (3 mL) and ionic liquid [BMIM][BF_4] (1 mL) was stirred at 100 °C for 3-4 h. At the end of reaction (monitored by TLC), the mixture was diluted with water (15-20 mL). The crude solid was filtered and washed with water and then recrystallized with 95 % EtOH to provide the pure products **4** (Table-1).

TABLE-1
SYNTHESIS OF 2,4,5-TRIARYLIMIDAZOLES **4**[a]

Comp.	R	Time (h)	Yield (%)	m.p. (ºC)
4a	2-NO_2-3-Cl	3	94	275-277
4b	4-Cl	3.5	96(95[16])	260-261(262-263[16])
4c	4-CN	3.5	95(84[16])	264-266(259-261[16])
4d	2-Br	3.5	96(71[17])	196-198(201-202[17])
4e	2-OCH_3	3	92(93[18])	203-205(208-210[18])
4f	2,4-$(OCH_3)_2$	3.5	90(98[19])	231-232(233-234[19])
4g	3-Br	3.5	94(85[18])	290-292(292-294[18])
4h	2-OH	4	92(93[20])	204-206(205[20])

[a]Reaction condition: aromatic aldehyde (1 mmol), benzil (1 mmol), ammonium acetate (5 mmol) and acetic acid (3 mL) in [BMIM][BF_4] (1 mL) at 100 ºC

General process of luminescence determination: The $CHCl_3$ solution of product **4a-4h** (1×10^{-6} mol/L) were measured on ultraviolet and fluorescence spectrophotometer to give their absorption and emission spectra, respectively (Table-2).

TABLE-2
LUMINESCENCE OF PRODUCTS

Product	R	λex (nm)	λem (nm)	Stokes (nm)	RFI	Φs[a]
4a	2-NO_2-3-Cl	256	403	147	8	0.32
4b	4-Cl	333	379	46	2316	0.03
4c	4-CN	345	444	99	565	0.45
4d	2-Br	308	387	79	396	0.30
4e	2-OCH_3	312	380	68	308	0.21
4f	2,4-$(OCH_3)_2$	311	393	82	376	0.11
4g	3-Br	312	379	67	1518	0.35
4h	2-OH	279	302	23	102	0.20

[a]The fluorescence quantum yields (Φ) were measured in $CHCl_3$ using quinine sulfate in 0.05 mol/L of sulfate acid aqueous solution (Φ = 0.55) as standard, Φs = (Φr × Fs × As)/(Fr × Ar)

Spectral data for compounds

2-(3-Chloro-2-nitrophenyl)-4,5-diphenyl-1*H*-imidazole (4a): m.p. 275-277 ºC; IR (KBr, ν_{max}, cm^{-1}): 3330, 1575, 1680, 1600; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.12-8.19 (13H, m, Ar-H), 12.95 (1H, s, N-H).

2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole (4b): m.p. 260-261 ºC; IR (KBr, ν_{max}, cm^{-1}): 3315, 1650, 1610; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.21-7.49 (14H, m, Ar-H), 13.26 (1H, s, N-H).

4-(4,5-Diphenyl-1*H*-imidazol-2-yl)benzonitrile (4c): m.p. 264-266 ºC; IR (KBr, ν_{max}, cm^{-1}): 3295, 2245, 1650, 1600; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.16-7.75 (14H, m, Ar-H), 12.81 (1H, s, N-H).

2-(2-Bromophenyl)-4,5-diphenyl-1*H*-imidazole (4d): m.p. 196-198 ºC; IR (KBr, ν_{max}, cm^{-1}): 3395, 1630, 1615; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.06-7.58 (14H, m, Ar-H), 12.91 (1H, s, N-H).

2-(2-Methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (4e): m.p. 203-205 ºC; IR (KBr, ν_{max}, cm^{-1}): 3300, 1650, 1600, 1250; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 6.16-7.65 (14H, m, Ar-H), 3.62 (3H, s, OCH_3), 12.88 (1H, s, N-H).

2-(2,4-Dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole (4f): m.p. 231-232 ºC; IR (KBr, ν_{max}, cm^{-1}): 3340, 1625, 1210; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 6.68-7.48 (13H, m, Ar-H), 3.75 (6H, s, OCH_3), 12.69 (1H, s, N-H).

2-(3-Bromophenyl)-4,5-diphenyl-1*H*-imidazole (4g): m.p. 290-292 ºC; IR (KBr, ν_{max}, cm^{-1}): 3345, 1640, 1590; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.21-7.65 (14H, m, Ar-H), 13.11 (1H, s, N-H).

2-(4,5-Diphenyl-1*H*-imidazol-2-yl)phenol (4h): m.p. 204-206 ºC; IR (KBr, ν_{max}, cm^{-1}): 3610, 3465, 1690, 1600; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 6.68-7.54 (14H, m, Ar-H), 8.21 (1H, s, O-H), 12.91 (1H, s, N-H).

RESULTS AND DISCUSSION

In this paper, it was found that the electronic nature and steric effect of substituted group in aromatic aldehyde have slight effect on this reaction. The luminescence properties of products were shown in Table-2. From Table-2, we can clearly see that: (1) Compared with the fluorescence emission of quinine sulfate (in 0.05 mol/L of sulfate acid aqueous solution) at 385 nm, the emission of **4a** and **4c** moved to 403 and 444 nm, respectively, the blue-shifted $\lambda_{max\ (ex)}$ of them means that they can emit stronger fluorescence than quinine sulfate. (2) The electro and steric effect of substituted group on aromatic aldehydes have large influence on the fluorescence properties. It seems that electron-donoring group in any position is not the favourable group which give poor fluorescence quantum yield (**4e**, **4f**, **4h**). The possible reason is that the two phenyls in **4-** and **5-** position are strong electron-donoring group, if another electron-donoring one is introduced into the imidazole ring, the molecule can not act as a classic D-π-A molecule to display strong fluorescence. (3) Besides **4b**, other products with electron-withdrawing group (**4a**, **4c**, **4d**, **4g**) exhibited stronger fluorescence with more than half fluorescence

quantum yield of quinine sulfate ($\Phi r = 0.55$, $CHCl_3$), which showed their potential application as new fluorescent probe or luminescence material.

Conclusion

In summary, this new protocol provides an environmentally benign route along with the associated advantages of simplicity of operation and higher atomic efficiency. So, we hope our efforts can provide some supports for the synthesis of substituted imidazoles and give some supplements for the applied range of ionic liquid [BMIM][BF_4]. The investigation of products' luminescence-structure relationship indicated that if we wish to develop 2-aryl-4,5-diphenylimidazoles as luminescence material, introduce electron-donoring group in 4'-position of 2-aryl in imidazole ring is the reasonable choice.

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