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FULL-LENGTH PAPER

Wells–Dawson heteropolyacid supported on silica: a highly efficient catalyst for synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles

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Abstract Heteropolyacid $H_6P_2W_{18}O_{62}\cdot 24H_2O$ (WD) supported on silica (WD/SiO_2) has been used as an effective catalytic system for the synthesis of various 1,2,4,5-tetrasubstituted imidazoles by four-component condensation of benzil, aldehydes, amines and ammonium acetate under solvent-free conditions. This approach can be useful for three-component synthesis of 2,4,5-trisubstituted imidazoles. The same reactions were repeated by using benzoin instead of benzil.

Keywords 2,4,5-Trisubstituted imidazoles · 1,2,4,5-Tetrasubstituted imidazoles · Wells–Dawson · Benzil · Benzoin

Introduction

Imidazoles are the core structures of many biological systems [1], viz. histidine, histamine and biotin, an active component in several drug molecules [2] (e.g. Losartan, Olmesartan, Eprosartan, and Trifenagrel), pesticides, and [3] have received a lot of attention in recent years. Different substituted imidazoles show a broad range of biological activities such as anti-inflammatory activity [4], anti-allergic activity [5], and analgesic activity [6]. In addition, many of the substituted diaryl imidazoles are known as potential inhibitors of the p38 MAP kinase [7]. Among these imidazoles, 2,4,5-triphenylimidazoles can be used as light-sensitive materials in photography, as inhibitors of IL-1 or p38 MAP kinase, fungicides and herbicides, plant growth regulators [8], and other type of therapeutic agents. Appropriately substituted imidazoles are extensively used as glucagon receptors [9] and CB1 cannabinoid receptor antagonists [10], modulators of P-glycoprotein (P-gp)-mediated multidrug resistance (MDR) [11], antibacterial [12], and antitumor [13] agents. Since tri- and tetrasubstituted imidazoles have become increasingly useful and important in the pharmaceutical fields, the development of clean, high-yielding, and environmentally friendly synthetic approaches are still desirable and much in demand. However, despite intensive efforts, only a handful of general methods exist for the construction of tri- and tetrasubstituted imidazoles.

Recently, the synthesis of these imidazoles has been catalyzed by silica gel or Zeolite HY [14], silica gel/$NaHSO_4$ [15], molecular iodine [16], $K_5CoW_{12}O_{40}\cdot 3H_2O$ [17], $H_3PW_{12}O_{40}$ [18], $HClO_4-$ SiO_2 [19], $Yb(OTf)_3$ [20], $NdCl_3$ [20], $LaCl_3$ [20], $FeCl_3$ [20], $AlCl_3$ [20], Al_2O_3 [21], $NiCl_2$ [22], $[HBim]BF_4$ [23], $InCl_3\cdot 3H_2O$ [24], ionic liquid [25], silica sulfuric acid [26], $BF_3\cdot SiO_2$ [27], ytterbium perfluorooctanesulfonate ($Yb(OPf)_3$) [28], $Zr(acac)_4$ [29], and tetrabutylammonium bromide [30].

Although these methods have a lot of potential, the reactions suffer from low yields, longer reaction times, use of expensive reagents, use of solvents, and toxic agents associated with a mixture of products and lack of generality, thus they were not suitable for, or were not applied for, the synthesis of structurally diverse imidazoles. Moreover, the synthesis of these heterocyclic compounds has usually been carried out in polar solvents such as ethanol, methanol, acetic acid, DMF, and DMSO, which leads to complex isolation and recovery procedures. Hence, the development of clean, high-yielding, and environmentally benign approaches is still desirable and much in demand.

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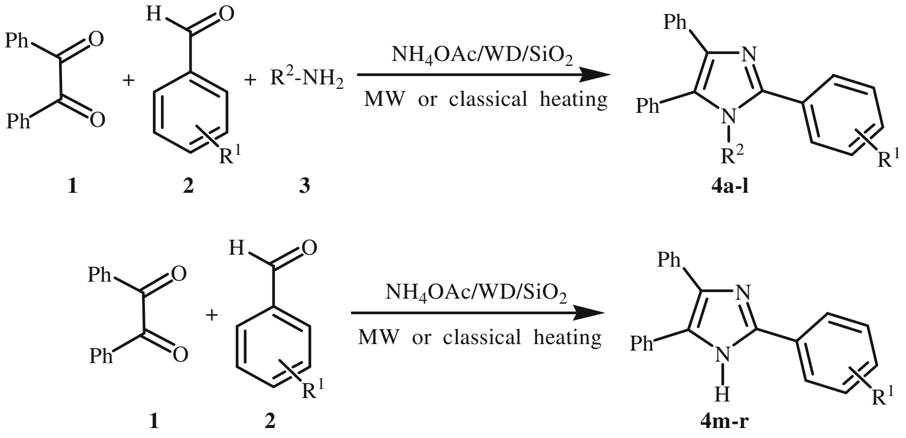
Scheme 1 Synthesis of highly substituted imidazoles by using of benzil



Solid acid-supported reagents are unique acid catalysts that have become popular over the last two decades. Since the activity and selectivity of a reagent dispersed on the surface of the support is improved as the effective surface area of reagent is greatly increased, they are expected to perform better than the individual reagents [31]. Low toxicity, moisture, air tolerance, and low price are other common features making the use of solid-supported reagents an attractive alternative to the conventional Lewis acids and triflates.

Although silica-support Keggin-type heteropolyacids have been widely studied as heterogeneous catalysts for various organic transformations [32], the majority of catalytic applications of the Wells–Dawson type polyoxoanions are devoted to homogeneous [33], or gas phase applications [34] and there are only a limited number of studies in heterogeneous systems carried out by using silica as a support [35].

Heteropolyacids (HPAs) have many advantages and are economically and environmentally attractive in both academic and industrial settings. They are useful acids and oxidation catalysts in various reactions since their catalytic features can be varied at a molecular level [34,36]. Until now, most of the research concerning physicochemical and catalytic properties of heteropolyacids (HPA) has been carried out using dodecaheteropolyacids of a Keggin structure. Only in the recent years have octadecaheteropolyacids of a Wells–Dawson structure attracted interest; reports are found increasingly in the literature, mainly of studies with $H_6P_2W_{18}O_{62}{\cdot}24H_2O$. A review of their catalytic properties and applications was published by Briand et al. [37]. The Wells–Dawson type heteropolyacids possess super-acidity and a remarkable stability both in solution and in the solid state [38]. Many typical acid-catalyzed reactions, including tetrahydropyranylation of alcohols [36], synthesis of coumarins [39], esterification [40], synthesis of β-acetamido ketones, and esters [41] are all effective in the presence of a suitable Wells–Dawson type heteropolyacid catalyst. To the best of our knowledge, there are no examples of the use of Wells–Dawson type heteropolyacids as catalyst for this type of synthesis of imidazole compounds.

In continuation to our previous study on the applications of solid supports for the development of new synthetic methodologies [15,42] and heterocyclic compounds containing nitrogen [15,42], and due to the resulting pharmacological interest in compounds which belong to the imidazole family, in this article we wish to report the solvent-free synthesis of tri- and tetrasubstituted imidazoles **4a-r** using a Wells–Dawson catalyst supported on silica gel under microwave irradiation or classical heating (Scheme 1).

Results and discussion

In this study, we present a study carried out using a Wells–Dawson HPA ($H_6P_2W_{18}O_{62}{\cdot}24H_2O$) supported on silica. The HPA with this structure has not been previously studied in the synthesis of highly substituted imidazoles. After some experimentation with respect to the catalytic amount of WD ($H_6P_2W_{18}O_{62}{\cdot}24H_2O$) and reaction temperatures, the optimal conditions have been established (Table 1). The acid is deposited on a macroporous support in order to minimize diffusional problems. The loading was varied between 10 and 30 wt%. The catalyst was tested in the four-component condensation of benzil, *p*-chlorobenzaldehyde, *p*-choloroaniline, and ammonium acetate as a model reaction. This reaction was also performed in the bulk WD acid where the WD was not supported; however, the yields of **4a** were low (Table 1, entry 1).

Table 1 shows that the three WD/SiO_2 supported catalysts are active for the production of **4a**. The behavior of the WD(20) and WD(30) is very similar, having a higher activity than the WD(10) (Table 1, entries 2–4). The effect of temperature was studied by carrying out the model reaction at different temperatures with WD/SiO_2 supported catalyst. It was observed that yields increased as the reaction temperature was raised (Table 1, entries, 3, 5–7). The imidazole

Table 1 Optimization for the synthesis of **4a**

Entry	Catalyst[a]	Temp. (°C)	Yield (%)[b]
1	Bulk WD	140	60
2	WD(10)/SiO_2	140	65
3	WD(20)/SiO_2	140	85
4	WD(30)/SiO_2	140	80
5	WD(20)/SiO_2	80	40
6	WD(20)/SiO_2	100	64
7	WD(20)/SiO_2	120	75

[a] The loading was varied between 10 and 30 wt%
[b] Yields refer to isolated products; reaction time: 2 h

product was found to be optimal both under microwave irradiation or classical heating but the microwave conditions afforded the product in shorter reaction times. The catalyst activity could be directly related to the number of surface acid sites accessible to the reactants. Therefore, the higher activity of the supported Dawson acid is directly correlated to an increment in the number of acidic sites for the supported samples [43].

A diverse set of imidazoles was synthesized with these optimized conditions (Table 2). The reactions proceeded in high yields and the method is effective with both aliphatic and aromatic amines. Aldehydes containing various functional groups such as Cl, NO_2, CH_3, and OMe were well tolerated and the reaction proceeded smoothly with high yields.

Generally, the synthetic procedure involves heating a mixture of WD/SiO_2, ammonium acetate (ammonia source) ben-

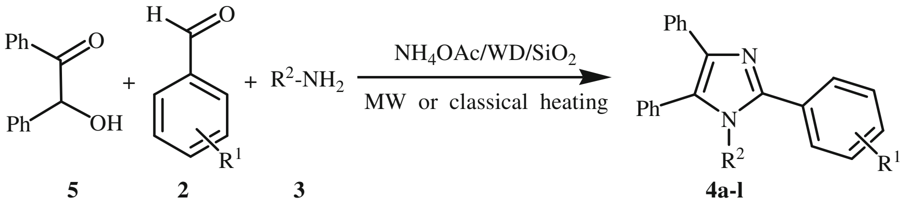
Table 2 Synthesis of **4a-r** from benzil catalyzed by (WD/SiO_2)[a]

4a-l	R^1	R^2	Yield (%)[d]	M.p. (°C)	Lit. M.p. (°C)
4a	*p*-Cl	4-Chlorophenyl	87[b] 85[c]	188–189	187–189 [15]
4b	*m*-NO_2	4-Methylphenyl	85[b] 82[c]	148–151	149–151 [15]
4c	*p*-NO_2	4-Methylphenyl	85[b] 85[c]	218–220	219–220 [15]
4d	*p*-Me	Benzyl	87[b] 85[c]	156–157	155–157 [15]
4e	*p*-Cl	Benzyl	90[b] 91[c]	157–158	156–158 [15]
4f	*p*-Cl	4-Florophenyl	86[b] 85[c]	196–198	196–198 [15]
4g	*m*-Cl	Benzyl	90[b] 91[c]	144–145	144–146 [15]
4h	*p*-Me	4-Methylphenyl	90[b] 89[c]	187–190	188–191 [15]
4i	*p*-Me	4-Chlorophenyl	90[b] 89[c]	166–168	167–169 [15]
4j	*p*-Me	Methyl	92[b] 85[c]	209–211	208–211 [15]
4k	*p*-Me	Ethyl	84[b] 90[c]	125–126	124–126 [15]
4l	*p*-Me	*iso*-Butyl	91[b] 88[c]	152–154	151–153 [15]
4m	H	H	90[b] 85[c]	274–276	275 [15]
4n	*p*-Me	H	93[b] 89[c]	228–229	233 [15]

Table 2 continued

4a-l	R^1	R^2	Yield (%)[d]	M.p. (°C)	Lit. M.p. (°C)
4o	*p*-Cl	H	88[b] 90[c]	258–260	261–263 [15]
4p	*p*-OMe	H	91[b] 88[c]	227–229	230–232 [15]
4q	*p*-NO_2	H	85[b] 90[c]	236–238	240 [15]
4r	*m*-NO_2	H	90[b] 90[c]	312–314	313–315 [15]

[a] The loading was 20 wt%
[b] MW (reaction time: 10 min)
[c] Classical heating (140°C, reaction time: 2 h)
[d] Yields refer to isolated products



Scheme 2 Synthesis of highly substituted imidazoles using benzoin

zil, aldehyde, and amine (Scheme 1). The results were excellent in terms of yields and product purity in the presence of WD/SiO_2 as shown in Table 2.

Under the same conditions, this approach can be repeated for the synthesis of imidazoles **4a-l** when the benzoin **5** was used as a starting material (Scheme 2). Thus, benzoin participated in the condensation with the aldehyde, amine, and ammonium acetate to give the corresponding tetrasubstituted imidazoles **4a-l** (Table 3). The results indicate that WD/SiO_2 is a better catalyst than $K_5CoW_{12}O_{40}{\cdot}3H_2O$.

The claim is justified through a few representative examples of four-component condensation in which the efficiency of WD/SiO_2 has been compared with recently reported catalysts (Table 4). The reaction of 4-methyl benzaldehyde, benzyl amine, benzil, and ammonium acetate was used as a model reaction.

The synthesis of 2,4,5-trisubstituted imidazoles by three-component condensation of benzil, aldehydes, amines, and ammonium acetate via the various catalytic systems is given in Table 5. The reaction of benzaldehyde, benzil, and ammonium acetate was used as a model reaction.

As it can be observed, our catalyst has comparable catalytic activity with respect to other catalytic systems. This method not only affords products in excellent yields under solvent free conditions, but it also is non-volatile, recyclable, non-explosive, easy to handle, and thermally robust. Moreover, when the benzoin was used as a starting material the yield of **4a-l** was increased in our catalytic system with respect to $K_5CoW_{12}O_{40}{\cdot}3H_2O$ (Table 3).

In summary, this article describes a convenient and efficient process for the synthesis of tri- and tetrasubstituted imidazoles through the three or four component coupling of benzil or benzoin, aldehydes, amine, and ammonium acetate using WD/SiO_2 as a solid acid. The present methodology offers very attractive features such as reduced reaction times, higher yields, and economic viability of the catalyst when

Table 3 Synthesis of **4a-l** from benzoin catalyzed by (WD/SiO_2)[a]

4a-l	R^1	R^2	Yield (%)[d]	Yield (%)[e]
4a	*p*-Cl	4-Chlorophenyl	33[b] 44[c]	20 30
4b	*m*-NO_2	4-Methylphenyl	33[b] 41[c]	15 25
4c	*p*-NO_2	4-Methylphenyl	29[b] 40[c]	15 30
4d	*p*-Me	Benzyl	33[b] 38[c]	18 30
4e	*p*-Cl	Benzyl	31[b] 43[c]	20 25

Table 3 continued

4a-l	R^1	R^2	Yield (%)[d]	Yield (%)[e]
4f	*p*-Cl	4-Florophenyl	27[b]	20
			37[c]	30
4g	*m*-Cl	Benzyl	25[b]	15
			39[c]	30
4h	*p*-Me	4-Methylphenyl	33[b]	30
			42[c]	30
4i	*p*-Me	4-Chlorophenyl	29[b]	20
			37[c]	25
4j	*p*-Me	Methyl	24[b]	–
			30[c]	
4k	*p*-Me	Ethyl	21[b]	–
			28[c]	
4l	*p*-Me	*iso*-Butyl	21[b]	–
			26[c]	

[a] The loading was 20 wt%

[b] MW (reaction time: 12 min)

[c] Classical heating (140°C, reaction time: 3 h)

[d] Yields refer to isolated products

[e] $K_5CoW_{12}O_{40}\cdot 3H_2O$ as catalyst [17]

Table 4 Comparison of the efficiency of various catalysts in the synthesis of tetrasubstituted imidazoles

Entry	Catalyst	Conditions	Time (min)	Yield (%)	Ref.
1	WD/SiO_2	140°C	120	85	This study
		MW	10	87	
2	BF_3/SiO_2	140°C	120	92	[28]
3	$HClO_4{-}SiO_2$	140°C	20	90	[19]
4	Zeolite HY	MW	6	85	[14]
5	$AlCl_3$	140°C	120	53	[28]
6	$MgCl_2$	140°C	120	50	[28]
7	$SnCl_4$	140°C	120	60	[18]
8	$H_3PW_{12}O_{40}$	Ethanol/reflux	15	88	[28]
9	$SiO_2/NaHSO_4$	140°C	120	92	[15]
		MW	12	96	
10	$K_5CoW_{12}O_{40}\cdot 3H_2O$	140°C	120	95	[17]
		MW	2	97	

Table 5 Comparison of the efficiency of various catalysts in the synthesis of trisubstituted imidazoles

Entry	Catalyst	Conditions	Time	Yield (%)	Ref.
1	WD/SiO_2	140°C	120 min	85	This study
		MW	10 min	90	
2	$InCl_3\cdot 3H_2O$	MeOH/RT	498 min	82	[25]
3	$Yb(OPf)_3$	$C_{10}F_{18}$/80°C	360 h	97	[29]
4	TBAB	Isopropanol/reflux	20 min	95	[31]
5	$NiCl_2\cdot 6H_2O/Al_2O_3$	Ethanol/reflux	25 min	94	[22]
6	$[HeMIM]BF_4$	100°C	120 min	88	[26]
		MW	2 min	93	
7	$Yb(OTf)_3$	HOAc/70°C	120 min	95	[20]
8	$SiO_2/NaHSO_4$	MW	6 min	90	[15]

compared with the conventional method as well as with the other catalysts and will have a wide scope in organic synthesis. The simple procedure, combined with ease of recovery and reuse of this catalyst, makes this method an economical, benign, and waste-free chemical process for the synthesis of tetrasubstituted imidazoles.

Experimental

Mps were measured on an Electrothermal 9100 apparatus. IR spectra were measured on a Unicom Galaxy Series FTIR 5000 Spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were determined on a Bruker Avance 300 MHz spectrometer. Elemental analyzes were performed using a Vario EL III elemental analyzer. Microwave irradiation was carried out in a National oven, model 5250, at 2450 MHz.

Preparation of the Wells–Dawson heteropolyacid supported on silica

The silica gel supported $H_6P_2W_{18}O_{62}{\cdot}24H_2O$ (WD acid) was prepared by mixing silica gel (1.5 g, Merck grade 60, 230–400 mesh) with a solution of WD acid (0.30 g) in distilled water (10 mL). The resulting mixture was stirred for 30 min and after removal of water in a rotary evaporator, the solid powder was dried at 70°C for 3 h.

General procedure for the preparation of products

A mixture of benzil (0.5 mmol) or benzoin, aldehyde (0.5 mmol), amine (0.5 mmol), and ammonium acetate (3 mmol) and 0.3 g of the WD/SiO_2 was thoroughly mixed in a mortar and it was irradiated in a domestic microwave oven at 600 W for 10–12 min or heated in the oil bath at 140°C for 2–3 h. The contents were cooled to room temperature and mixed thoroughly with 3×10 ml of acetone. The solid inorganic material was filtered off. After separation of solid, the solvent was evaporated under reduced pressure. The resulting solid residue was purified by recrystallization from acetone–water (15:1 v:v).

The 2,4,5-trisubstituted imidazoles **4m-r** were prepared as described for the **4a-l** by three-component reaction of benzil, aldehydes, and ammonium acetate.

All products are known compounds and were characterized by IR and ^{1}H-NMR spectroscopies, and their melting points are compared with the reported values [15,22]. All products gave satisfactory spectral data in accord with the assigned structures [e.g. for **4a** and **4r**, 1,2-Bis(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (**4a**): M.p. 188–189°C; IR (KBr) (ν_{max}/cm^{-1}): 1601, 1495, 1414; ^{1}H-NMR (DMSO-d_6, 300 MHz) δ_H: 2.21 (s, CH_3), 6.91–7.63 (m, 18H$_{arom}$) ppm. And 2-(3-nitrophenyl)-4,5-diphenyl-1*H*-imidazole (**4r**): mp: 312–314°C, IR (KBr) (ν_{max}, cm^{-1}): 3417, 3048, 1532, 1519, 1345; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ_H: 7.36–8.96 (14H, m, H$_{arom}$), 12.93 (1H, bs, NH).

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