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A new catalyst for the synthesis of 2-substituted perimidines catalysed by FePO₄

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Abstract

The reaction of 1,8-diaminonaphthalene with aromatic aldehydes gave 2-substituted perimidines in the presence of FePO₄ as a versatile, green and reusable catalyst at room temperature.

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Keywords: Synthesis; 2-Aryl-2,3-dihydro-1H-perimidines; Catalyst; FePO₄

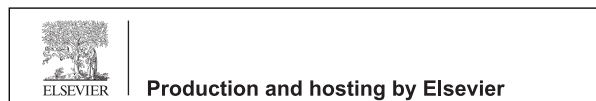
1. Introduction

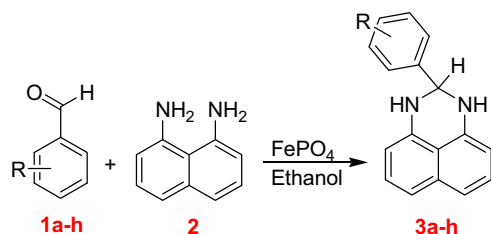
Multinuclear N-heterocyclic compounds, such as perimidines, are of wide interest because they exhibit a diverse range of biological activities [1]. Due to their biological activities, there are several preparative methods for the synthesis of perimidines [2–7]. The most commonly method for the preparation of perimidines is the condensation reaction of 1,8-diaminonaphthalene with a carbonyl group, which requires a special reagent or force reaction conditions. However, because of the continuing interest in this field, investigation into simple methods for the synthesis of perimidines is important. Recently, the use of an inorganic solid acid in

organic synthesis has become more popular [8–12]. In addition to the cases mentioned above, FePO₄ is an inexpensive, safe and available reagent [13] that has also been employed for the selective oxidation of CH₄ to CH₃OH [14] and benzene to phenol [15], one-pot synthesis of dihydropyrimidinones and thiones [16], one-pot three component synthesis of 2,4,5-trisubstituted imidazoles [17], synthesis of 1,2,4,5-tetraarylated imidazoles [18], acetylation of alcohols and phenols with acetic anhydride [19], synthesis of bis(indolyl)methanes [20], synthesis of 1,2-disubstituted benzimidazoles [21] and synthesis of 2-disubstituted benzimidazoles [22]. In addition, a part of our programme is aimed at developing selective and environmental friendly methodologies for the preparation of fine chemicals [17–21]; due to the versatile biological properties of perimidines and as a continuation of our studies on the synthesis of heterocyclic compounds, we report a clean and simple synthetic method for the preparation of perimidines using FePO₄ as an efficient catalyst, which was employed as green catalyst for the reaction between 1,8-diaminonaphthalene and aromatic aldehydes at ambient temperature. The attractive features of this procedure are

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Scheme 1. Synthesis of 2-substituted perimidines using FePO₄.

a good conversion and reusability of the catalyst and an easy work up (Scheme 1).

2. Results and discussion

Initially, to ascertain a suitable condition, the reaction of 1,8-diaminonaphthalene with benzaldehyde in the presence of FePO₄ was performed in various solvents, such as water, ethanol, acetonitrile and dimethylsulphoxide. Ethanol was found to be the most effective solvent for this reaction. The results are shown in Table 1.

To establish the optimum amount of the catalyst needed for this reaction, various ratios of FePO₄ were examined using benzaldehyde (1.0 mmol) and 1,8-diaminonaphthalene (1.0 mmol) at room temperature as a model reaction (Table 1). Any desired products were not obtained in the absence of the catalyst over 24 h, and the best yields were obtained with 10 mol% of FePO₄ in 12 h. Thus, the catalyst is an essential component for the synthesis of 2-phenyl-2,3-dihydro-1*H*-perimidine (Table 2).

To generalize the model reaction, the reactions were performed at room temperature for the time indicated in Table 3 by taking a 1:1 molar ratio mixture of 1,8-diaminonaphthalene and the aromatic aldehyde in the presence of FePO₄ in ethanol to give 2,3-dihydro-1*H*-perimidines in suitable yields. As observed from the results presented in Table 3, aromatic aldehydes containing both electron-withdrawing groups (NO₂, Cl) and electron-donating groups (Me, OH) reacted

Table 1

Optimization of the varying solvents for the synthesis of 2-phenyl-2,3-dihydro-1*H*-perimidine.

Entry	Solvent (5 ml)	Yield % ^a
1	Ethanol	95
2	Water/ethanol (30/70)	90
3	Acetonitrile	70
4	DMSO	70

^a Condition: Benzaldehyde (1.0 mmol), 1,8-diaminonaphthalene (1.0 mmol) and FePO₄ (10 mol%) at room temperature.

Table 2

Optimization of the catalyst amount for the synthesis of 2-phenyl-2,3-dihydro-1*H*-perimidine.

Entry	Catalyst (mol%)	Yield % ^a
1	0	–
2	1	60
3	5	80
4	10	95

^a Condition: Benzaldehyde (1.0 mmol), 1,8-diaminonaphthalene, ethanol (5 ml), ethanol and FePO₄ at room temperature.

smoothly to produce high product yields. Aromatic aldehydes with electron-withdrawing groups showed an increased reaction rate (Table 3). A reasonable pathway for the formation of 2-substituted perimidines in the presence of FePO₄ is disclosed in Scheme 2. Nucleophilic attack of 1,8-diaminonaphthalene **2** to FePO₄-activated aldehyde **1** afforded intermediate **3** following intermediate **4**. In situ dehydration of compound **4** and intramolecular nucleophilic attack of the second amino group to FePO₄-activated imine intermediate **5** obtained intermediate **6** to produce the desired compound **7**.

3. Conclusion

In conclusion, we developed a simple, rapid, efficient and green method based on the use of a heterogeneous and reusable catalyst accompanied by the use of ethanol as a solvent due to its low cost, environmentally friendly nature and convenient synthetic method for the synthesis of biologically important perimidines catalyzed by FePO₄. The reaction conditions are mild, and the reaction gives excellent product yields. In addition, to show the advantages of using FePO₄ as a solid catalyst in the synthesis of 2-phenyl-2,3-dihydro-1*H*-perimidine, our protocol was compared with previously reported methods (Table 4). From the results given in Table 4, the advantages of this work are evident regarding the good yield, easy separation and reusability of the catalyst.

4. Experimental

Mps were measured by using the capillary tube method with an electro thermal 9200 apparatus. The IR spectra were recorded using a Perkin Elmer FT-IR spectrometer scanning between 4000 and 400 cm⁻¹. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker DRX-500 MHz in CDCl₃. Analytical TLC of

Table 3
 Synthesis of 2-substituted pyrimidines using FePO₄.

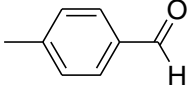
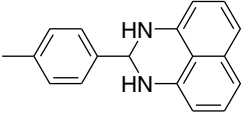
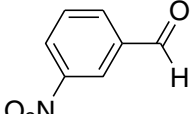
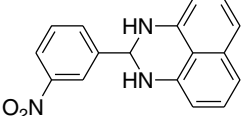
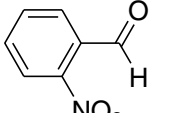
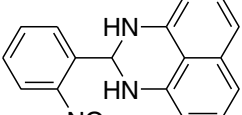
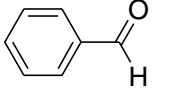
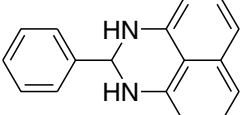
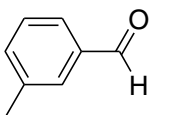
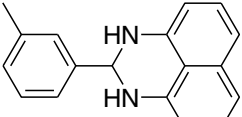
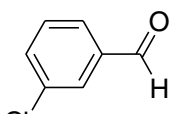
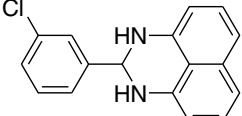
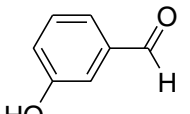
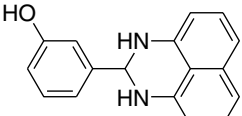
Entry	Aldehyde	Product	Time (h)	Yield %	M.P. (°C)	
					Found	Reported [ref.]
1	 1a	 3a	15	80%	160–161	163 [11,23]
2	 1b	 3b	7.0	90%	188–190	190 [23,10]
3	 1c	 3c	8.0	85%	158–160	160 [23,9]
4	 1d	 3d	12	80%	100–101	103 [12]
5	 1e	 3e	15	78%	160–161	163 [10,11]
6	 1f	 3f	10	85%	116–118	116 [9,13]
7	 1g	 3g	16	80%	188–189	189 [9,10]

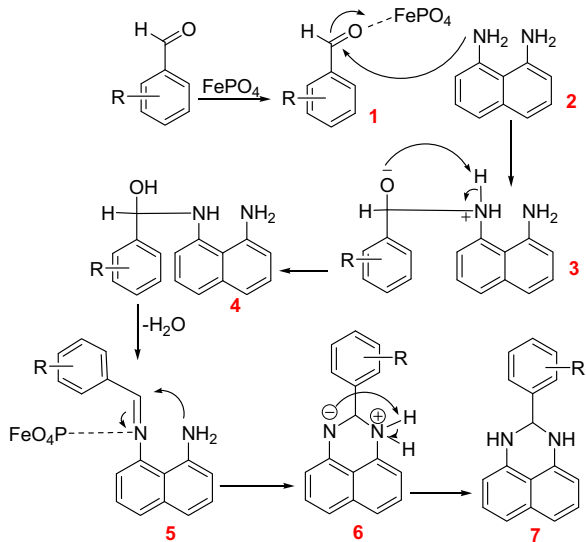
Table 3 (Continued)

Entry	Aldehyde	Product	Time (h)	Yield %	M.P. (°C)	
					Found	Reported [ref.]
8			10	80%	158–160	160 [10,9]

Table 4

Synthesis of 2-phenyl-2,3-dihydro-1H-perimidine catalyzed by various catalysts.

Entry	Catalyst	Solvent	Time	Yield%	Ref.
1	CuY-zeolite	EtOH	25 min/RT	81	[24]
2	Fe ₃ O ₄ /SiO ₂ /(CH ₂) ₃ N + Me ₃ Br ₃ core-shell nanoparticles	No solvent	12 min/80 °C	93	[25]
3	AcOH	EtOH	24 h/RT	52	[26]
4	Ytterbium(III) trifluoromethanesulphonate	MeCN	24 h/RT	88	[27]
5	I ₂	EtOH	40 min/RT	84	[28]
6	NaY zeolite	EtOH	45–50 h/RT	70	[23]
7	Cu(NO ₃) ₂ ·2H ₂ O	EtOH	10 min/RT	83	[29]
8	FePO ₄	EtOH	12 h/RT	80	This work

Scheme 2. Proposed mechanism of the FePO₄-catalysed synthesis of 2-substituted perimidines.

all reactions was performed on Merck precoated plates (silica gel 60F-254 on aluminium).

4.1. General procedure for preparation of 2-arylperimidines

To a solution of 1,8-diaminonaphthalene (1 mmol) and aromatic aldehyde (1 mmol) in ethanol (5 ml),

FePO₄ (10 mol%, 0.01 g) was added. The mixture was stirred at room temperature for appropriate times (Table 1). After the completion of the reaction, the catalyst was separated by filtration, ethanol was evaporated and the solid product was observed.

4.2. Recycling of the catalyst

After the completion of the reaction, hot ethanol (10 ml) was added to the reaction mixture, and then, the catalyst was separated by filtration. The precipitate was washed with hot ethanol and then air dried for the catalyst recovery study. The catalyst was reused for the synthesis of 2-phenyl-2,3-dihydro-1H-perimidine three times (80, 80, 78)%.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jtusci.2015.10.004](https://doi.org/10.1016/j.jtusci.2015.10.004).

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