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Arabian Journal of Chemistry

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ORIGINAL ARTICLE

PTA ($\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$): An eco-friendly catalyst for the synthesis of new Schiff-bases containing benzimidazole moiety

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Received 27 May 2011; accepted 22 July 2011

KEYWORDS

Benzimidazole derivatives;
3-Amino-2-naphthoic acid;
Schiff's base derivatives;
Aldehydes;
 $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$

Abstract In this study $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$ is found to catalyze the preparation of Schiff bases from the reaction of 3-(1*H*-Benzimidazol-2-yl)naphthalene-2-amine with different aldehydes efficiently in ethanol. The advantages of this environmental friendly and mild method are such as simplicity of the reaction procedure, the elimination of solvents, simple work-up, high product yields and short reaction times. The products were characterized by FT-IR ^1H NMR, ^{13}C NMR, mass spectrometry and elemental analysis.

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1. Introduction

In recent years, the use of heterogeneous catalysts have received considerable interest in various disciplines, including organic synthesis owing to their easy work-up procedures, easy filtration, commercially available, environmentally friendly, minimization of cost and no effluent generation due to recycling of these catalysts (Gadekara et al., 2009; Clark, 2002; Alizadeh et al., 2003). The applications of heterogeneous catalyst, especially heteropolyacids have become most important for the development of environmentally benign chemical processes and technologies in green chemistry (Heravi et al., 2008; Clark, 2001; Anastas and Warner, 1998). Heteropolyacids have been found to act as outstanding catalysts in electrophilic transformation. They are stronger than the usual mineral acids, such as HCl, H_2SO_4 and HNO_3 (Heravi and Sadjadi, 2009). Among the heteropolyacids, PTA is the most widely used catalyst, because of its high acid strength, thermal stabilities and low reducibilities (Devassy et al., 2004).

Benzimidazole ring plays an important heterocyclic pharmacophore in drug discovery. These compounds carrying out different substituents in benzimidazole structure are associated with a wide range of biological activities including anticancer (Kruse et al., 1989), antiviral (Townsend, 1996), antimicrobial (Hubschwerlen et al., 1992), antihelminthic (Veerakumari and Munuswamy, 2000), anti-inflammatory (Labanauskas et al., 2000), antihistaminic (Iemura et al., 1986), proton pump inhib-

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Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2011.07.030



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itor (Kuhler et al., 1988), antioxidant (Cole et al., 1974), anti-hypertensive (Kubo et al., 1993) and anticoagulant (Mederski et al., 2004) properties. These derivatives also exhibit significant activity against several viruses such as HIV (Porcari et al., 1998; Roth et al., 1997).

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, e.g., biological, inorganic and analytical chemistry (Cimerman et al., 2000; Singh et al., 1975; Perry et al., 1988). They are reported to show characteristic biological activities including antibacterial, antifungal, anticancer, anti-convulsant anti-inflammatory activities (Jarrahpour et al., 2006; Taggi et al., 2002a,b; Chohan et al., 2006; Pandeya et al., 1999; Pathak et al., 2000; Samadhiya and Halve, 2001). Other applications of Schiff's bases include industrial synthesis of high value life saving beta lactam Taggi et al., 2002a,b antibiotics from a class of penicillins and cephalosporins. Owing to the importance of PTA and in continuation of our work on the development of eco-friendly reactions, we report synthesis of new Schiff bases containing benzimidazole moiety with various aromatic aldehydes by using PTA as an eco-friendly catalyst.

2. Results and discussions

In the present protocol, we are reporting a simple method for the synthesis of Schiff's base from substituted 3-(1*H*-Benzimidazol-2-yl) naphthalene-2-amine. Initially substituted 3-(1*H*-Benzimidazol-2-yl) naphthalene-2-amine is synthesized by the reaction of 3-amino-2-naphthoic acid and substituted *o*-phenylenediamine in the presence of PTA as catalyst to afford substituted 3-(1*H*-Benzimidazol-2-yl) naphthalene-2-amine. Later the free NH₂ was condensed with various aldehydes to give Schiff bases. The purity of the synthesized compounds was checked by performing TLC. Using optimized reaction parameters, Schiff base derivatives (**a11–a20**) were synthesized. The time required and the yield of the products is given in Table 1. In each case, condensation of substrates occurred and upon work-up, the corresponding Schiff base was obtained. As seen in Table 1, a lot of Schiff bases were synthesized using PTA as a catalyst in ethanol.

The reaction proceeds rapidly with 5 mol% of catalyst and is complete within 2 h. In a control experiment, it was observed that in the absence of the catalyst, reaction did not proceed even at higher temperatures. It is of great importance that the reaction is largely affected by the PTA catalyst. The entries 3 and 9, (Table 1) respectively, show the reaction of *p*-nitro-

Table 1 The reaction of amine with various aldehydes catalyzed by H₃PO₄·12WO₃·xH₂O in Ethanol.

Entry	R ¹	Time (h)	Compounds	Yield (%)	m.p. (°C)
1	H	3	a11	83	142–144
2	2-Cl	2	a12	79	196–197
3	2-NO ₂	3	a13	42	140–141
4	3-Cl	2.5	a14	79	178–180
5	4-OCH ₃	1.5	a15	69	156–158
6	H	2	a16	83	121–122
7	4-OCH ₃	2	a17	66	104–106
8	2-Cl	1.5	a18	80	75–76
9	2-NO ₂	3	a19	46	106–108
10	3-Cl	3	a20	82	133–134

Table 2 Solvent effect on the synthesis of Schiff bases.^a

Entry	Solvents	Time (h) ^b	Yield (%) ^c
1	DMF	12	43
2	1,4-Dioxane	14	58
3	THF	8	38
4	Methanol	7	51
5	DMSO	26	60
6	Ethanol	1.5	95

^a The mixture of 3-(1*H*-Benzimidazol-2-yl) naphthalene-2-amine and benzaldehyde using PTA as catalyst in different solvents.

^b Time to finish the reaction monitored by TLC.

^c Yield refers to isolated products.

benzaldehyde with 3-(1*H*-benzo[d]imidazole-2-yl)naphthalene-2-amine and the reaction of *p*-nitro-benzaldehyde with 3-(6-methyl-1*H*-benzo[d]imidazole-2-yl)naphthalene-2-amine under reflux in ethanol solution with long reaction times, the corresponding products were obtained in low yields. This low yield may be related to steric hindrance in benzaldehyde accompanied to electron withdrawing of nitro group on aromatic ring of aldehyde.

In order to evaluate the effect of the solvent, reaction was carried out with 3-(1*H*-Benzimidazol-2-yl) naphthalene-2-amine and benzaldehyde using PTA as a model reaction (Table 2). When the reaction was performed in ethanol using PTA as catalyst, the reaction was very fast and the product was easily isolated from the reaction mixture. The model reaction was also performed using different solvents like DMF, 1,4-dioxane, THF, methanol, DMSO (Table 2). But the yields were low and the reaction times were too long. These results suggest that ethanol is the best solvent for this method.

The structures of the synthesized compounds were determined on the basis of their FT-IR and ¹H NMR data and elemental analysis. The IR spectra of the synthesized compounds showed the presence of C=N stretching bands around 1687–1612 cm⁻¹ and NH stretching frequencies appear in the range of 3435–3324 cm⁻¹ corresponding to azomethine compounds. In the ¹H NMR spectra of the target schiff's base, the –NH proton of imidazole ranges from 9.71–11.04 ppm. While N=CH proton varies from 4.38–4.57 ppm. The other protons appeared at the expected chemical shifts.

3. Conclusions

In conclusion, a successful attempt has been made to synthesize Schiff's base derivatives from corresponding substituted 3-(1*H*-Benzimidazol-2-yl) naphthalene-2-amine and various aldehydes using ethanol as solvent in high yields. The method employed is very simple and economically viable.

4. Experiments

4.1. Methods and materials

All compounds were routinely checked by thin-layer chromatography (TLC) on aluminum-backed silica gel plates. Melting points were determined with open capillary method and are uncorrected. IR spectra were recorded on a Nicolet 5700 FT-IR instrument (Nicolet, Madison, WI, USA) as KBr discs. The ¹H-NMR and ¹³C-NMR spectra were measured with a

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