

An efficient catalytic synthesis of 1,2-dihydro-1-aryl-3*H*-naphth[1,2-*e*][1,3]oxazin-3-one derivatives using silica supported Preyssler heteropolyacid, H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂ (50%) as a heterogeneous catalyst

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Silica supported Preyssler type heteropolyacids are found to be efficient catalysts for the synthesis of 1,2-dihydro-1-aryl-3*H*-naphth[1,2-*e*][1,3]oxazin-3-one derivatives in good yields in a convenient, efficient and green reaction by condensation of β -naphthol, aromatic aldehydes, urea, and ethanol under reflux conditions. The catalyst is recycled and reused several times.

Keywords: Preyssler; heteropolyacid; naphtho-oxazine; aromatic aldehyde; catalyst.

INTRODUCTION

Naphthalene-condensed 1,3-oxazin-2-ones have been reported to act as antibacterial agents [1]. They have been used as precursors in the preparation of phosphinic ligands for asymmetric catalysis [2]. Sodium hydrogen sulphate (NaHSO₄), n-tetrabutylammonium bromide (TBAB) as a phase transfer catalyst (PTC) in water, and 1-butyl-3-methyl imidazolium hydrogen sulphate ([bmim]HSO₄) as ionic liquid (IL) have been used as mild reaction promoters for the cyclocondensation of formaline, β -naphthol and aromatic amines to afford the respective 2,3-dihydro-2-phenyl-1*H*-naphtho-[1,2-*e*] [1,3] oxazine derivatives [3]. 1,2-Dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-one derivatives were synthesized in high yields using a facile one-pot condensation of 2-naphthol, aromatic aldehydes and urea catalyzed by perchloric acid supported on silica under thermal solvent-free conditions [4]. 1,2-Dihydro-1-phenyl-naphtho [1,2-*e*] [1,3] oxazin-3-one derivatives were prepared in good yields using a novel one-pot reaction involving β -naphthol, urea and aromatic aldehydes under solvent-free conditions [5]. Hitherto, only few reports for the synthesis of naphthalene-condensed oxazinone derivatives have been documented in the literature. Aromatic oxazines were first synthesized in 1944 by Holly and Cope through Mannich reactions from phenols, formaldehyde, and amines [6]. From the

1950s to the 1960s, many benzoxazines and naphthoxazines were synthesized by Burke and co-workers [7]. Fulop *et al.* reported the condensation of amino alkyl naphthols as precursors with phosgene in the presence of triethylamine giving naphthalene - condensed 1,3 - oxazin - 2 - one derivatives in moderate yields [8]. Cimarelli and co-workers used carbonyl di-imidazole instead of phosgene for the synthesis of these compounds [9]. Polyoxometalates (POMs) are attracting much attention as building blocks for functional composite materials because of their interesting nanosized structures [10–12]. This interest has resulted in the development of numerous protocols for the synthesis of nanostructured materials over a range of sizes. However, in spite of the extensive investigations on the synthesis and characterization of Keggin-type nanocatalysts [13–14], the synthesis of sodium 30-tungstophosphate nanocatalysts has been largely overlooked.

In our attempt to use POMs as catalysts in organic reactions, we reported that Preyssler-type heteropolyacid [NaP₅W₃₀O₁₁₀]¹⁴⁻ shows good catalytic reactivity [15–21]. We were encouraged by our recent success in working with POMs as green catalysts, and by the research in the field of nanotechnology [22–23]. In the last decades, heteropolyacids (HPAs) and related polyoxometalate compounds have attracted much attention as economically and environmentally friendly catalysts [24–32]. HPAs have very strong Brønsted acidity, approaching the superacid range; moreover, they are efficient oxidants. HPAs are very soluble in polar solvents such as water,

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alcohols, ketones, *etc.* Therefore, HPAs are employed in homogeneous systems as acid and oxidation catalysts and, particularly, they show higher catalytic activity than mineral acids [22, 26, 29]. On the other hand, HPAs are non-toxic and mildly to non-corrosive, so they are generally recognized as clean and safe catalysts.

EXPERIMENTAL

Materials

All chemicals were purchased from Merck Company. Melting points were measured by the capillary tube method with an Electrothermal 9200 apparatus. All reactions were followed using Kieselgel 60 F256 TLC.

INSTRUMENTS

¹H NMR spectra were recorded on a Bruker AQS AVANCE-300 MHz spectrometer using TMS as an internal standard (DMSO solution). IR spectra were recorded in KBr disks on the FT-IR Bruker Tensor 27. Mass spectra were recorded using a MS 5973 Network Mass Selective detector. All products were characterized by ¹H NMR, FTIR, mass spectra and melting point.

Preparation of the silica supported Preyssler heteropolyacid catalyst, H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂, (H₁₄-P₅/SiO₂), (50% catalyst loading):

H₁₄[NaP₅W₃₀O₁₁₀], (H₁₄-P₅) was prepared by passing a solution of the potassium salt in water through a column (50 cm × 1 cm) of Dowex 50W×8 in the H⁺ form and evaporating the eluate to dryness under vacuum. The supported heteropolyacid catalyst was synthesized according to our previous report [18] by impregnating the support (SiO₂ powder) with an aqueous solution of H₁₄[NaP₅W₃₀O₁₁₀], (H₁₄-P₅). After stirring the mixture, the solvent was evaporated, dried at 120 °C and was calcined at 250 °C in a furnace prior to use.

GENERAL EXPERIMENTAL PROCEDURE

A mixture of an appropriate β-naphthol (2 mmol), aldehyde (2 mmol), urea (0.03 mol), silica supported Preyssler heteropolyacid, H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂ (50% catalyst loading) as a catalyst (0.07 g) and C₂H₅OH (10 mL) was heated under reflux for a properiate time. The progress of the reaction was monitored by TLC. Then the

reaction mixture was filtered for separating the heterogeneous heteropolyacid catalyst and the reaction mixture was poured onto crushed ice, extracted with ethyl acetate and washed with water. The ethyl acetate extract was dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was re-crystallized from CH₂Cl₂.

SPECTRAL DATA:

1-phenyl-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (5a):

m.p. 216–218 °C, IR (KBr, cm⁻¹) ν_{\max} : 3295, 1730, 1517; ¹H NMR (300 MHz, DMSO-*d*₆) δ_{H} : 6.17 (d, 1H, J = 2.1 Hz, CH), 7.76 (m, 11H, Arom.), 8.85 (s, 1H, NH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ_{C} : 54.22, 114.50, 117.30, 123.54, 125.53, 127.42, 127.81, 128.47, 129.08, 129.30, 129.41, 130.68, 130.86, 143.32, 147.85, 149.77; MS (m/z, %): 275 (M⁺, 7), 231 (100), 202 (35). Anal. calcd for C₁₈H₁₃NO₂: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.57; H, 4.71; N, 5.14.

1,2-Dihydro-1-(4-chlorophenyl)-3H-naphth[1,2-e][1,3]oxazin-3-one (5b):

m.p. 209–210 °C, IR (KBr, cm⁻¹) ν_{\max} : 3222, 3145, 1734; ¹H NMR (300 MHz, DMSO-*d*₆) δ_{H} : 6.22 (1H, s, CH), 7.79 (10H, m, Arom.), 8.90 (1H, s, NH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ_{C} : 53.40, 114.01, 117.32, 123.50, 125.60, 127.92, 128.06, 129.13, 129.23, 129.37, 129.42, 130.85, 133.06, 142.20, 147.90, 149.60; MS (m/z, %): 309 (M⁺, 5), 265(60), 231(100), 202(27). Anal. calcd for C₁₈H₁₂NO₂Cl: C, 69.80; H, 3.90; N, 4.52. Found: C, 69.86; H, 3.84; N, 4.48.

1-(4-fluorophenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (5c):

m.p. 201–203 °C, IR (KBr, cm⁻¹) ν_{\max} : 3134, 2952, 1755; ¹H NMR (300 MHz, DMSO-*d*₆) δ_{H} : 5.96 (1H, d, J = 3 Hz, CH), 7.71 (m, 10H, Arom.), 8.61 (d, 1H, J = 2.7 Hz, NH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ_{C} : 53.37, 114.28, 116.05, 116.35, 117.33, 123.50, 125.58, 127.86, 129.11, 129.56, 130.83, 139.58, 147.86, 149.69, 160.40, 163.65; MS (m/z, %): 294 (M⁺+1, 15), 249 (100), 231(10), 220 (25). Anal. calcd for C₁₈H₁₂FNO₂: C, 73.71; H, 4.12; N, 4.78. Found: C, 73.75; H, 4.07; N, 4.72.

1-(4-bromophenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (5d):

m.p. 218–220°C, IR (KBr, cm⁻¹) ν_{\max} : 3145, 1732; ¹H NMR (300 MHz, DMSO-*d*₆) δ_{H} : 6.24 (s, 1H, CH), 7.79 (m, 10H, Arom.), 8.90 (s, 1H, NH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ_{C} : 53.55, 113.93, 117.32, 121.65, 123.47, 125.61, 127.90, 129.12, 129.22, 129.68, 130.86, 132.34, 142.60, 147.90, 149.60; MS (m/z, %): 353 (M⁺, 25), 309 (100), 230 (100), 200 (100). Anal. calcd for C₁₈H₁₂NO₂Br: C, 61.04; H, 3.41; N, 3.95. Found: C, 61.07; H, 3.44; N, 3.91.

1-(2-chlorophenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (5e):

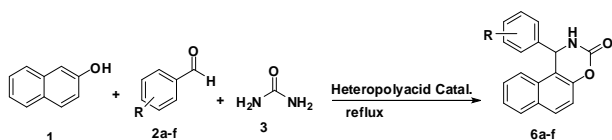
m.p. 250–252°C, IR (KBr, cm⁻¹) ν_{\max} : 3219, 3140, 1728; ¹H NMR (300 MHz, DMSO-*d*₆) δ : 6.51 (1H, s, CH), 7.67 (m, 10H, Arom.), 8.90 (s, 1H, NH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ_{C} : 52.15, 112.96, 117.30, 122.72, 125.58, 128.09, 128.80, 129.25, 129.32, 130.28, 130.51, 130.87, 131.10, 132.15, 139.95, 148.27, 149.13; MS (m/z, %): 309 (M⁺, 9), 283(17), 231(100). Anal. calcd for C₁₈H₁₂NO₂Cl: C, 69.80; H, 3.90; N, 4.52. Found: C, 69.76; H, 3.85; N, 4.50.

1-(3-bromophenyl)-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (5f):

m.p. 225–227°C, IR (KBr, cm⁻¹) ν_{\max} : 3140, 1730; ¹H NMR (300 MHz, DMSO-*d*₆) δ_{H} : 6.25 (1H, s, CH), 7.89 (m, 10H, Arom.), 8.93 (s, 1H, NH); ¹³C NMR (100 MHz, DMSO-*d*₆) δ_{C} : 53.47, 113.75, 117.36, 122.47, 123.48, 125.68, 126.30, 128.0, 129.15, 129.24, 130.39, 130.87, 131.01, 131.43, 131.77, 145.77, 148.01, 149.63; MS (m/z, %): 353 (M⁺, 18), 310 (63), 231 (100). Anal. calcd for C₁₈H₁₂NO₂Br: C, 61.04; H, 3.41; N, 3.95. Found: C, 61.07; H, 3.45; N, 3.98.

RESULTS AND DISCUSSION

A convenient, efficient and green method for the synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-ones is reported (Scheme 1).



Scheme 1. Synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-ones using a H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂ catalyst (50% catalyst loading).

The reaction of β -naphthol, benzaldehyde and urea in the presence of silica supported Preyssler heteropolyacid catalyst was investigated at appropriate times under reflux conditions (Table 1). We found that the reaction proceeds efficiently and with good yields with the aldehydes (1–5) having electron-withdrawing substituents, but the reaction yields were lower when the aldehydes (6–7) having electron-donating substituents (benzaldehydes) were used (Table 1). According to the proposed mechanism, this reaction was considered to proceed through the acylium intermediate (4) (formed by reaction of the aldehyde (2) with urea (3) and H⁺ of the Preyssler heteropolyacid catalyst) and the subsequent reaction of the β -naphthol (1) with the acylium (4), affording the product (5). At a high temperature, the product (5) underwent cyclization to afford the products (5a–f) (Scheme 2).

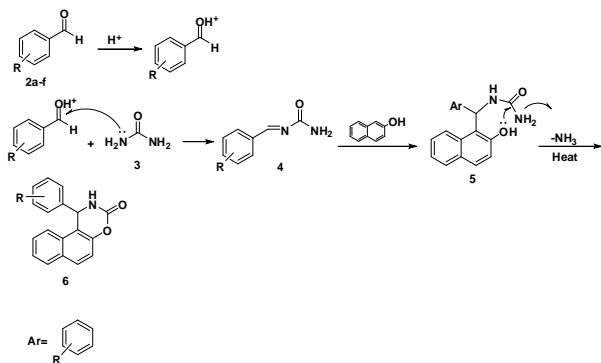
Table 1. Results of the synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-ones using H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂ (50% catalyst loading) under reflux conditions

Entry	Aldehyde	Time (min)	^a Yield (%)
1		31	85
2		35	92
3		40	80
4		45	82
5		55	80
6		130	70.5
7		120	72
8		60	91

^aIsolated yield.

The work-up procedure of this reaction is very simple. After completion of the reaction, the mixture was filtered off to separate the catalyst and the solvent was evaporated to dryness under reduced pressure. The pure products were obtained by re-crystallization from CH₂Cl₂.

Scheme 2. Mechanism of the synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-ones



REUSABILITY OF THE CATALYST

At the end of the reaction, the catalyst could be recovered by simple filtration. The recovered catalyst was washed with dichloromethane and dried at 130 °C for 1 h. The recycled catalyst was used for other reactions without appreciable loss in its catalytic activities (Table 2). In addition, as a non-hygroscopic, non-corrosive and water stable solid acid, this catalyst is easily handled and suitable for large-scale operation. The reaction appears to be heterogeneously catalyzed. High yields, relatively short reaction times, simplicity of operation and easy work-up procedure are some other advantages of this protocol.

Table 2. Reusability of silica supported Preyssler heteropolyacid catalyst, H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂ (50% catalyst loading) in the synthesis of 1-phenyl-1H-naphtho[1,2-e][1,3]oxazin-3(2H)-one (Table 1, entry 8).

Entry	Number of recycles	Time (min)	^a Yield (%)
1	1	60	90
2	2	60	89
3	3	60	87
4	4	60	84

^aIsolated yield

CONCLUSIONS

In conclusion, we have described a very simple and convenient procedure for the synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-one

derivatives catalyzed by the non-corrosive, and environmentally benign (green) Preyssler type heteropolyacid. Also, the catalyst is recyclable and could be reused without significant loss of activity. Even after four reaction runs, the catalytic activity of H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂ (50% catalyst loading) was almost the same as that of the freshly used catalyst.

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ЕФЕКТИВЕН КАТАЛИТИЧЕН СИНТЕЗ НА 1,2- ДИХИДРО-1-АРИЛ-3Н-НАФТ[1,2-*E*][1,3]ОКСАЗИН-3-ОН ПРОИЗВОДНИ ПРИ ИЗПОЛЗВАНЕ НА ХЕТЕРОПОЛИКИСЕЛИНА НА НОСИТЕЛ СИЛИЦИЕВ ДИОКСИД $H_{14}[NAP_5W_{30}O_{110}]/SiO_2$ (50%) КАТО PREYSSLER ХЕТЕРОГЕНЕН КАТАЛИЗАТОР

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(Резюме)

Установено е, че хетерополикиселини тип Preyssler върху силициев диоксид са ефективен катализатор при синтеза на 1,2- дихидро-1-арил-3Н-нафт[1,2-*e*][1,3]оксазин-3-он производни с добър добив чрез удобна, ефективна и зелена реакция при кондензация на β - нафтол ароматни алдехиди, уреа и етанол при условия на отвеждане. Катализаторът се рециклира и използва отново няколко пъти.