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ORIGINAL ARTICLE

Aqua mediated SnO_2 nanoparticles: A recyclable and benign catalyst for the synthesis of Quinoxalines

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Abstract

An efficient and mild synthesis of quinoxalines including cyclo-condensation of 1, 2-phenylenediamine and 1, 2-diketonesin the presence of1mol% catalytic amount of SnO2 nanoparticles (1 mol%) in water at room temperature is established. On the whole, this study introduced at this point is substantial in terms of using water as solvent, low reaction time(5 to 10 minutes), high yields of products (85-88%), reusability of catalyst(three cycles), eco-friendliness, effortlessness of performance and it displays along the line of green chemistry.

Keywords: *Aqua Mediated SnO2 Nanoparticles; Cyclo-condensation; Quinoxalines; 1, 2-Diketones; 1, 2-Phenylenediamine.*

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INTRODUCTION

Lately, being focused on green chemistry by using environmentally mild reagents and conditions is one of the most attractive improvements in synthesis of broadly applied organic compounds. Therefore, the use of water as a favorable solvent for organic reactions has received significant attention [1-3]. Water is a valuable solvent in many methods and carrying out organic reactions in this medium is of great interest [4]. It is certainly the most low-cost among numerous solvents applied in organic synthesis. The absence of explosive, inflammable, mutagenic and carcinogenic properties is a satisfactory aspect of water in laboratories. Additionally, water is considered as one of the appropriate solvents from an eco-friendly point of opinion [5].

Due to developing green concerns, the progress of clean synthetic processes has become essential and serious investigation. For this reason, heterogeneous organic reactions have many advantages, for example recycling, comfort of handling separation and eco-friendly safe removal [6, 7].

Quinoxalines represent a substantial category of nitrogen heterocyclic compounds as they constitute valuable intermediates in organic synthesis and are appropriate dyes [8]. Some of them show biological activities containing antiprotozoal, anti-bacterial, anti-HIV, anti-inflammatory, anti-viral, antidepressant, anti-cancer and as kinase inhibitors [9-27]. In addition, they were displayed to be NMDA receptor antagonist, PDGF-RTK inhibitor, IL-8 receptor antagonist and5-HT_3receptor antagonist in the similar mode [28-33]. Several synthetic approaches and catalysts have been studied for the preparation of quinoxalines such as 6-amino-2,3-dichloroquinoxaline loaded on AMEBA resin [34], lead oxide [35], $(NH_4)_6Mo_7O_{24}.4H_2O$ [36], [PBBS] and [TBBDA] [37], $Zr(OTf)_4$ [38], silica bonded

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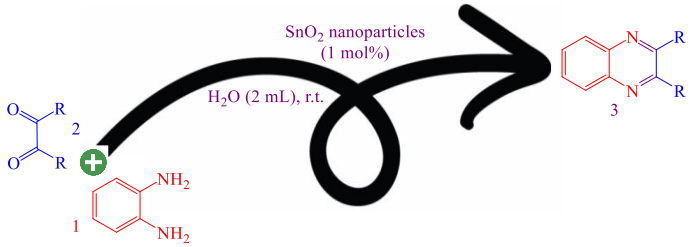
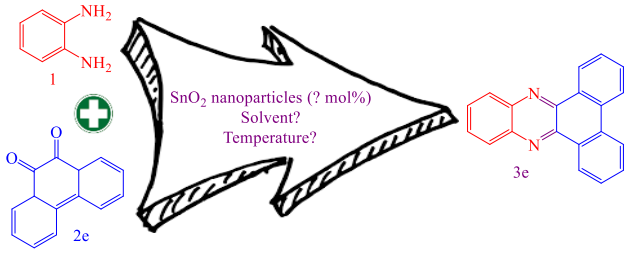


Fig. 1. Aqua mediated SnO_2 nanoparticles catalyzed synthesis of quinoxalines.

Table 1. Evaluation of catalytic activity and solvent in the synthesis of target molecule 3e.[a]



Entry	Solvent	Catalyst loading (mol%)	Time (min)	Yield (%)[b]
1	H_2O	1	5	88
2	C_2H_5OH	1	10	84
3	CH_2Cl_2	1	10	83
4	CH_3CN	1	10	82
5	H_2O	0.5	10	84
6	H_2O	2	10	83
7	H_2O	3	10	82

[a]Reaction condition: 1,2-phenylenediamine (1 mmol; 0.108 g), phenanthrene-9,10-dione (1 mmol; 0.208 g), solvent (2 mL), room temperature;

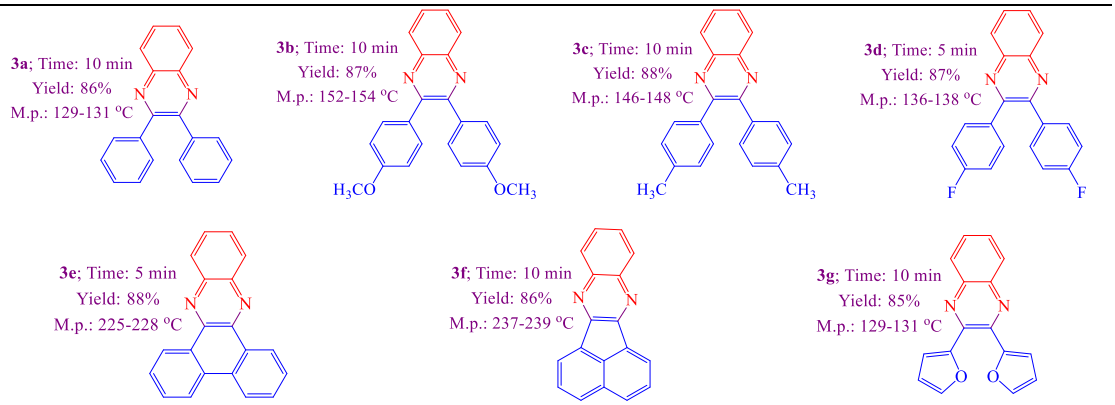
[b] Isolated yield.

S-sulfonic acid [39], solid-phase synthesis on Synphase™ Lanterns [40], nano-flake ZnO [41],$[MIMPS]_3PW_{12}O_{40}$, $[TEAPS]_3PW_{12}O_{40}$ [42], Basolites [43] and Porous carbons [44].

The investigation of metal oxides has attracted the consideration of materials experts because of their mechanical, electrical, magnetic, optical, catalytic suitable relations [45] and the removal of toxic metals and dyes [46], which make them scientifically valuable. The efficacy of metal nanoparticles as reagents or catalysts in chemistry has remarkable potential in organic synthesis and materials science [47-50]. Tin oxide is a significant material owing to its properties for example strong physical and chemical interaction with adsorbed species, low operating temperature, high degree of transparency in the visible spectrum and strong thermal stability in air (up to 500 °C) [51]. Furthermore, tin oxide is broadly applied in electrochemical properties [52] and catalysis field [53-58].

As part of our efforts to investigate the usefulness of nano metal oxide catalysts for the synthesis of organic and heterocyclic compounds [53-63], we report an efficient process for the synthesis of α quinoxalines from the cyclo-condensation reaction between 1, 2-phenylenediamine and 1, 2-diketones by using 1 mol% aqua mediated SnO_2 nanoparticles at room temperature (Fig. 1).

Table 2. Synthesis of quinoxalines catalyzed by SnO_2 nanoparticles.[a,b]



[a]Reaction condition: 1,2-phenylenediamine (1 mmol; 0.108 g), 1,2-diketone (1 mmol), SnO_2 nanoparticles (1 mol%), H_2O (2 mL), room temperature; [b] Isolated yield.

MATERIALS AND METHODS

General methods

SnO_2 nanoparticles were purchased from commercial centers and characterized by using various techniques [53-55, 63]. All reagents were purchased from Merck and Aldrich and applied without more purification. All solvents were reagent grade. All yields refer to the isolated products after purification. The selected products were identified by comparison with authentic samples and by using spectroscopic data include FT-IR spectra, ^{1}H NMR and ^{13}C NMR analyses and melting point. FT-IR spectra were recorded on FT-IR Bruker (WQF-510) spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-400 MHz by using TMS as the internal standard. All melting points were taken on a Thermo Scientific apparatus and were uncorrected. TLC was attained on aluminum sheets silica gel F_{254}.

General procedure for the synthesis of quinoxalines by using aqua mediated SnO_2 nanoparticles

To a mixture of 1, 2-phenylenediamine (1.0 mmol) and 1, 2-diketones (1.0 mmol) was added SnO_2 nanoparticles (1 mol%) in H_2O (2 mL). The mixture was stirred at room temperature for the known time (Table 2). The progress of the reaction was checked by TLC (*n*-hexane/ethyl acetate; 5 : 2). After completion of the reaction, water was removed and the product was heated in ethanol. SnO_2 nanoparticles was filtered (the product was soluble in hot ethanol and the catalyst was insoluble). Finally, the crude product was purified by recrystallized from ethanol to afford the pure product.

Spectral data for selected products

*2, 3-Diphenylquinoxaline (Table 2, **3a**)*: Yellow crystalline solid, M.p.: 129-131 °C; Yield: 86%; FT-IR (KBr) (υ_{max}, cm^{-1}): 2956, 1695, 1460, 1377; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.50-7.67 (dd, 4H, J_1 = 16 Hz and J_2 = 8.0 Hz, Ar–H), 7.92-7.94 (d, 2H, J = 8.0 Hz, Ar–H), 7.95-7.99 (dd, 4H, J_1= 16 Hz and J_2 = 8.0 Hz, Ar–H), 8.02-8.04 (d, 2H, J = 8.0 Hz, Ar–H), 8.69-8.71 (d, 2H, J = 8.0 Hz, Ar–H); ^{13}C NMR (100 MHz, DMSO-d_6): 148.5, 146.3, 131.2, 131.1, 130.1, 129.5, 129.1, 127.7.

*Dibenzo[a,c]phenazine (Table 2, **3e**)*: White crystalline solid, M.p.: 225-228 °C; Yield: 88%; FT-IR (KBr) (υ_{max}, cm^{-1}): 3051, 1601, 1475, 1354, 1221; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.73-7.75 (d, 2H, J = 8.0 Hz, Ar–H), 7.76-7.82 (dd, 2H, J_1 = 16 Hz and J_2 = 8.0 Hz, Ar–H), 7.84-7.88 (dd, 2H, J_1= 16 Hz and J_2 = 8.0 Hz, Ar–H), 8.31-8.36 (dd, 2H, J_1= 16 Hz and J_2 = 8.0 Hz, Ar–H), 8.51-8.56 (d, 2H, J = 8.0 Hz, Ar–H), 9.38-9.41 (d, 2H, J = 8.0 Hz, Ar–H); ^{13}C NMR (100 MHz, DMSO-d_6): 122.9, 126.2, 127.9, 129.4, 129.7, 130.2, 132.0, 142.2, 142.4, 146.3.

RESULTS AND DISCUSSION

Firstly, we studied the activity of SnO_2 nanoparticles in the cyclo-condensation of 1, 2-phenylenediamine and phenanthrene-9, 10-dione as a model reaction (Table 1). To our enchantment, the expected product **3e** was achieved in 88% isolated yield after5 minutes in

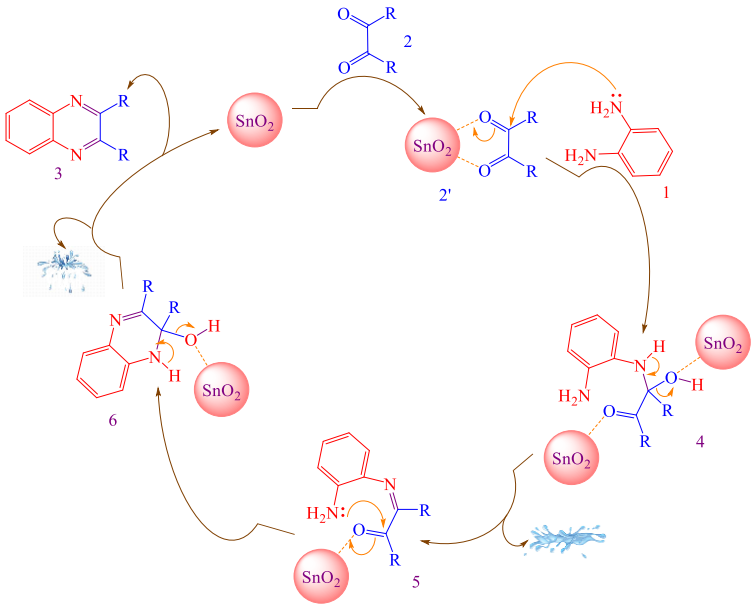


Fig. 2. Suggested mechanism for the synthesis of quinoxalines catalyzed by SnO_2 nanoparticles.

the presence of a 1 mol% catalytic amount of Aqua mediated SnO_2 nanoparticles at room temperature (Table 1, entry 1).No desired product was synthesized in the absence of SnO_2 nanoparticles.

It is identified that the reaction medium plays a significant role in the catalytic reaction. The investigation of the effect of the nature of solvent for this reaction by using SnO_2 nanoparticles was performed at room temperature in several solvents (Table 1, entries 1-4). The highest reaction activity was attained in the system by using water as a solvent in comparison to other solvents under same reaction conditions. The above model reaction was achieved under solvent-free condition with the SnO_2 nanoparticles to provide low yield.

Catalyst concentration is an important factor that fully affects the reaction rate and product yield. To optimize the catalyst loading, 0.5 mol%, 2 mol% and 3 mol% of SnO_2nanoparticleswas studied but the yields were not appropriate (Table 1, entries 5-7). A 1 mol% loading of SnO_2 nanoparticles was satisfactory to push the reaction forward and higher amounts of catalyst did not increase the yields meaningfully.

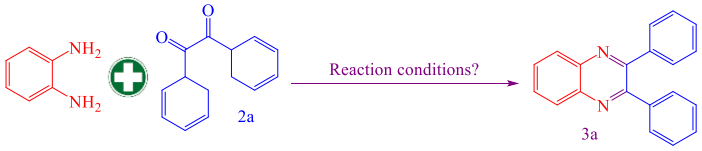
We next studied the effect of temperature on the rate of model reaction. For this aim, the reaction was performed in higher temperatures and under reflux condition. But, by increasing the temperature unsuccessful to improve the reaction rate significantly. As it happens, higher temperatures were lowered the product yield rather, attended by approximately impurities. Moreover, the appropriate result was attained with a 1 : 1 molar ratio for 1, 2-phenylenediamine and 9, 10-phenantrolinedione.

The SnO_2 nanoparticles catalyst could be recycled and reused without decrease of catalytic activity. At the end of the reaction, hot ethanol was added to the reaction mixture and SnO_2 nanoparticles was filtered (the product was soluble in hot ethanol and the catalyst was insoluble), washed three times with hot ethanol, dried at 80 °C for 120 minutes, and reused. The recycled catalyst was used to the synthesis of **3e** and the yield was reserved at 86-88% *via* three cycles of catalyst recovering.

To consider the scope and overview of the method, a variety of 1, 2-diketones bearing electroneutral and electron-releasing groups were reacted with 1, 2-phenylenediamine as nucleophilic substrates under optimized reaction conditions and the results are showed in Table 2. No apparent electronic effect of the substituents of 1, 2-diketones was obvious. The corresponding quinoxalines were produced efficiently with facility and suitable yields (85-88%).

The proposed mechanism for this reaction is displayed in Fig. 2 [37-39]. Initially, SnO_2nanoparticles as a catalyst activates the

Table 3. Comparison of this process with some other processes for the synthesis of 2,3-diphenylquinoxaline.



Entry	Reaction condition	Time (min)	Yield (%)	Reported reference
1	SnO_2 nanoparticles (1 mol%), H_2O, r.t.	10	86	This work
2	Et_4NBrO_3 (1 mmol), H_2O, r.t.	20	92	[64]
3	PbO (4 mmol), EtOH, 60 °C	55	95	[35]
4	$(NH_4)_6Mo_7O_{24}.4H_2O$ (2 mol%), $EtOH/H_2O$ (3/1, v/v), r.t.	15	95	[36]
5	Na_2CO_3 (0.6 mmol), PEG-400, r.t.	30	90	[65]
6	$Zr(OTf)_4$ (10 mol%), $EtOH/H_2O$ (3/2, v/v), r.t.	10	96	[38]
7	SBSSA (3.4 mol%), $EtOH/H_2O$ (70/30, v/v), r.t.	5	96	[39]
8	SBA-Pr-SO_3H (0.2 g), CH_2Cl_2, r.t.	10	95	[66]

carbonyl functional group of 1, 2-diketones **2** to give intermediate **2'**. At that point, nucleophilic attacks of 1, 2-phenylenediamine **1** on the intermediate **2'** to provide intermediate **4**. The condensation of intermediate **4** leads to the form of intermediate **5** *via* elimination of one molecule of water. In the next step, intra-cyclization of intermediate **5** *via* nucleophilic attack of amine group on the activated carbonyl functional group to afford intermediate **6** which rearranges through elimination of second molecule of water to quinoxalines **3**.

To display the noteworthy properties of our investigation, we have compared our result with the known data from the other works for the synthesis of 2, 3-diphenylquinoxaline (Table 2, 3a). For comparison, this target molecule was selected, as shown in Table 3. No use of hazardous solvent, short reaction time and high yields of target product make this process as a valuable method for the synthesis of library of quinoxalines.

CONCLUSION

In summary, we have introduced a facile and eco-friendly mild process for the synthesis of quinoxalines. This cyclo-condensation reaction between 1, 2-phenylenediamine and 1,2-diketones is efficiently catalyzed by aqua mediated SnO_2 nanoparticles at room temperature. Easy operation, improved rates, high isolated yields of the pure products and benign reaction conditions are important advantages of the procedure presented here. More uses of SnO_2 nanoparticles on the extension of this approach are continuing in our group.

SUPPORTING INFORMATION

The supporting information includes spectral images of FT-IR, ^1H NMR and ^{13}C NMR of selected product.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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