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Synthesis of 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ols) catalyzed by nanosilica supported perchloric acid in water

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ABSTRACT

Reaction between aromatic aldehydes and 3–methyl-1-phenyl-2-pyrazoline-5-one catalyzed by nano-SiO_2/$HClO_4$ in water under reflux provided a simple and efficient route for the synthesis of 4-((5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(aryl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol derivatives in high yields.

***Keywords**: Nano-SiO_2/$HClO_4$, Aromatic aldehydes, 3–Methyl-1-phenyl-2-pyrazoline-5-one, Water.*

1. Introduction

Pyrazoles and pyrazolones are important compounds that are known to possess multiple biological activities, with possess anti-anxiety, antipyretic and anti-inflammatory activities [1-5]. Furthermore, 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ols) have a broad spectrum of approved biological activity, such as anti-inflammatory [6], gastric secretion stimulatory [7], antidepressant [8] and antibacterial [9].

The synthesis of 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ols) has been reported in the presence of some catalyst such as ceric ammonium nitrate [10], sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester [11] and pyridine trifluoroacetate [12].

Application of environmentally benign water and solid acid catalyst represents powerful green procedure.
In this work, the application of solid phase acidic green nano catalyst (nano-SiO_2/$HClO_4$) have investigated for synthesis of 4,4´-(arylmethylene)bis (1*H*-pyrazol-5-ols).

2. Experimental

2.1. General

Melting points were determined with an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyzer at analytical laboratory of Science and Research Unite of Islamic Azad University. The morphologies of the nanoparticles were observed using SEM of a VEGA//TESCAN microscope with an accelerating voltage of 15 kV.

The chemicals for this work were purchased from Fluka and were used without further purification.

2.2. Synthesis of perchloric acid supported on silicagel nanoparticles

The reagent was prepared by combination of 70% aqueous $HClO_4$ (1.8 g, 12.5 mmol) and 23.7 g of nano silicagel in 70 mL diethyl ether were stirred for 3 h at room temperature.

The mixture was concentrated and the residue dried under vacuum at 100 °C for 72 h to afford nano-SiO_2/$HClO_4$ (0.5 mmol/g) as a free flowing power. The dimensions of nanoparticles were observed with SEM.

*2.3. General procedure for the preparation of compounds 3**a-m***

A mixture of 3–methyl-1-phenyl-2-pyrazoline-5-one (2 mmol), aromatic aldehyde (1 mmol), nano-SiO_2/$HClO_4$ (6 mg) and H_2O (5 mL) was placed in a round bottom flask. The materials were mixed and refluxed in water for the 20 min.

After completion of the reaction, the mixture was filtered to remove the catalyst. After evaporation of the solvent, the crude product was recrystallized from hot ethanol to obtain the pure compound.

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3. Results and Discussion

SEM image of nano-SiO_2 was shown in Fig. 1. The stable silicagel nanoparticles is prepared [13] and used for preparation of catalyst (nano-SiO_2/$HClO_4$).

Fig. 2 shows the SEM image of perchloric acid supported on silicagel nanoparticles. The size of particles are between 20-30 nm.

In continuation of previous research on the use of solid acids in organic synthesis [14-17], the synthesis of 4,4′-(arylmethylene) bis (1*H*-pyrazol-5-ols) have investigated by condensation of 3–methyl-1-phenyl-2-pyrazoline-5-one **1** and an aromatic aldehyde **2** in the presence of 6 mg nano-SiO_2/$HClO_4$ catalyst (Scheme 1).

To optimize the reaction conditions, the reaction of benzaldehyde and 3–methyl-1-phenyl-2-pyrazoline-5-one was used as a model reaction. Initially, the catalytic activity of nano-SiO_2/$HClO_4$ have compared with other catalysts, according to the obtained data, this catalyst afforded good yields however, have limitations of long reaction time, lower yields, greater amounts of catalyst and often expensive catalysts (Table 1, entries 1-7).

In order to determine the optimum quantity of nano-SiO_2/$HClO_4$, model reaction was carried out at reflux in water condition (Table1, entries 8-10). Nano-SiO_2/$HClO_4$ (6 mg) gave an excellent yield in 20min (Table1, entry 9). The above reaction was also examined in various solvents. The best results were obtained when water was used as a solvent at reflux (Table 1, entry 9).

To study the scope of the reaction, a series of aromatic aldehydes and 3–methyl-1-phenyl-2-pyrazoline-5-one catalyzed by nano-SiO_2/$HClO_4$ were examined. The results are shown in Table 2. In all cases, aromatic aldehyde substituted with either electron-donating or electron-withdrawing groups underwent the reaction smoothly and gave products in excellent yields. All products are known and were identified by their melting points, IR spectroscopy and elemental analyses.

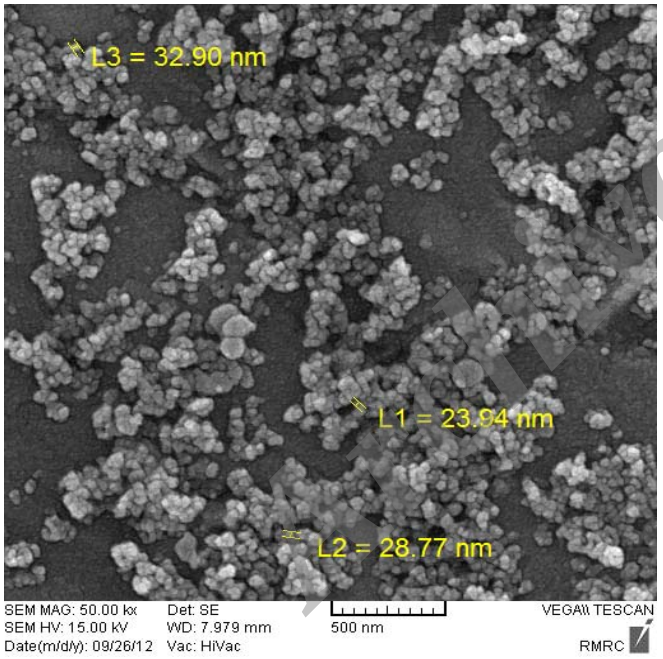


Fig 1. The SEM image of SiO_2 nanoparticles.

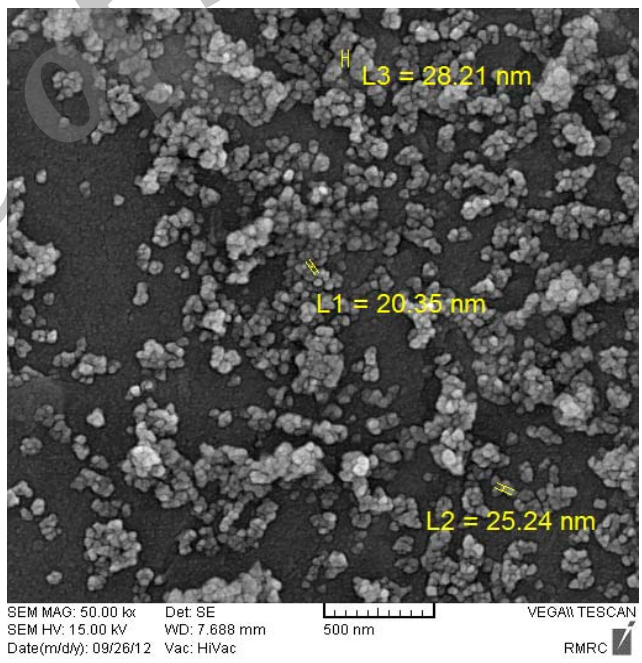
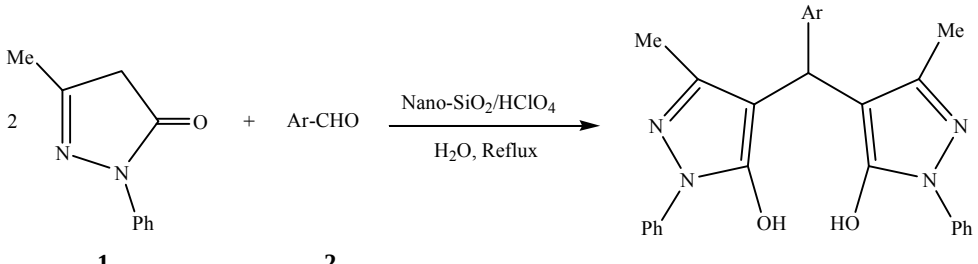


Fig. 2. The SEM image of nano-SiO_2/$HClO_4$.



1 **2** **3a-m**

Scheme 1. Condensation of aromatic aldehydes with 3–methyl-1-phenyl-2-pyrazoline-5-one by nano-SiO_2/$HClO_4$ as catalyst.

Table1. Comparison of the efficiency of nano-SiO_2/$HClO_4$ with reported catalysts for the synthesis of **3a** and optimization of the reaction condition.

Entry	Catalyst (amount)	Temp. (°C)	Solvent	Time (min)	Yield (%)[a]	Ref.
1	Ceric ammonium nitrate (5 mol%)	25	H_2O	15	92	[10]
2	SASPSPE[b] (100 mg)	80	EtOH	180	90	[11]
3	Nano-SiO_2/$SbCl_5$ (6 mg)	100	H_2O	20	84	-
4	Nano-SiO_2/BF_3 (6 mg)	100	H_2O	20	82	-
5	SiO_2/$HClO_4$ (6 mg)	100	H_2O	20	72	-
6	Nano-SiO_2 (6 mg)	100	H_2O	20	62	-
7	$HClO_4$ (6 mg)	100	H_2O	20	68	-
8	Nano-SiO_2/$HClO_4$ (4 mg)	100	H_2O	20	85	-
9	Nano-SiO_2/$HClO_4$ (6 mg)	100	H_2O	20	94	-
10	Nano-SiO_2/$HClO_4$ (8 mg)	100	H_2O	20	95	-
11	Nano-SiO_2/$HClO_4$ (6 mg)	80	EtOH	20	87	-
12	Nano-SiO_2/$HClO_4$ (6 mg)	40	CH_2Cl_2	20	83	-

[a]Isolated yield
[b]Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester.

Table 2. Nano-SiO_2/$HClO_4$ catalyzed the synthesis of 4,4′-(arylmethylene)bis(1*H*-pyrazol-5-ols).

Entry	Ar	Product	Yield (%)[a]	m.p. (°C)		Ref.
				Found	Reported	
1	C_6H_5	3a	94	171-172	170-171	[10]
2	2-BrC_6H_4	3b	86	199-200	198-200	[11]
3	4-FC_6H_4	3c	91	182-184	181-183	[11]
4	4-MeC_6H_4	3d	93	203-205	203-204	[10]
5	2-OHC_6H_4	3e	87	229-230	227-229	[11]
6	4-$OHCC_6H_4$	3f	85	214-215	214-216	[11]
7	4-CNC_6H_4	3g	91	208-210	210-212	[11]
8	3-$NO_2C_6H_4$	3h	94	152-153	151-153	[11]
9	4-$NO_2C_6H_4$	3i	96	224-226	225-227	[11]
10	2-ClC_6H_4	3j	83	236-237	235-237	[11]
11	4-ClC_6H_4	3k	91	217-218	215-217	[11]
12	2-Furfuryl	3l	95	189-191	189-190	[10]
13	2-Pyridyl	3m	94	230-232	232-233	[10]

[a]Isolated yield.

4. Conclusions

In summary, nano-SiO_2/$HClO_4$ has prepared as a new catalyst and shown that it has advantages in the preparation of 4,4′-(arylmethylene)bis(1H-pyrazol-5-ols) such as shorter reaction times, simple work-up, and affords excellent yield. The present method does not involve any hazardous organic solvent. Therefore, this procedure could be classified as green chemistry.

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