

Synthesis of 4,4'-(arylmethylene)bis(1H-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-SiO₂/HClO₄ in water under reflux provided a simple and efficient route for the synthesis of 4-((5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)(aryl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol derivatives in high yields.

Keywords: Nano-SiO₂/HClO₄, 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(1H-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(1H-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-SiO₂/HClO₄) have investigated for synthesis of 4,4'-(arylmethylene)bis(1H-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 Unit 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 HClO₄ (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-SiO₂/HClO₄ (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 3a-m

A mixture of 3-methyl-1-phenyl-2-pyrazoline-5-one (2 mmol), aromatic aldehyde (1 mmol), nano-SiO₂/HClO₄ (6 mg) and H₂O (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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Table 1. Comparison of the efficiency of nano-SiO₂/HClO₄ 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 ₂ O	15	92	[10]
2	SASPSPE ^b (100 mg)	80	EtOH	180	90	[11]
3	Nano-SiO ₂ /SbCl ₅ (6 mg)	100	H ₂ O	20	84	-
4	Nano-SiO ₂ /BF ₃ (6 mg)	100	H ₂ O	20	82	-
5	SiO ₂ /HClO ₄ (6 mg)	100	H ₂ O	20	72	-
6	Nano-SiO ₂ (6 mg)	100	H ₂ O	20	62	-
7	HClO ₄ (6 mg)	100	H ₂ O	20	68	-
8	Nano-SiO ₂ /HClO ₄ (4 mg)	100	H ₂ O	20	85	-
9	Nano-SiO ₂ /HClO ₄ (6 mg)	100	H ₂ O	20	94	-
10	Nano-SiO ₂ /HClO ₄ (8 mg)	100	H ₂ O	20	95	-
11	Nano-SiO ₂ /HClO ₄ (6 mg)	80	EtOH	20	87	-
12	Nano-SiO ₂ /HClO ₄ (6 mg)	40	CH ₂ Cl ₂	20	83	-

^aIsolated yield^bSulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester.**Table 2.** Nano-SiO₂/HClO₄ 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 ₆ H ₅	3a	94	171-172	170-171	[10]
2	2-BrC ₆ H ₄	3b	86	199-200	198-200	[11]
3	4-FC ₆ H ₄	3c	91	182-184	181-183	[11]
4	4-MeC ₆ H ₄	3d	93	203-205	203-204	[10]
5	2-OHC ₆ H ₄	3e	87	229-230	227-229	[11]
6	4-OHCC ₆ H ₄	3f	85	214-215	214-216	[11]
7	4-CNC ₆ H ₄	3g	91	208-210	210-212	[11]
8	3-NO ₂ C ₆ H ₄	3h	94	152-153	151-153	[11]
9	4-NO ₂ C ₆ H ₄	3i	96	224-226	225-227	[11]
10	2-ClC ₆ H ₄	3j	83	236-237	235-237	[11]
11	4-ClC ₆ H 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]

^aIsolated yield.

4. Conclusions

In summary, nano-SiO₂/HClO₄ 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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