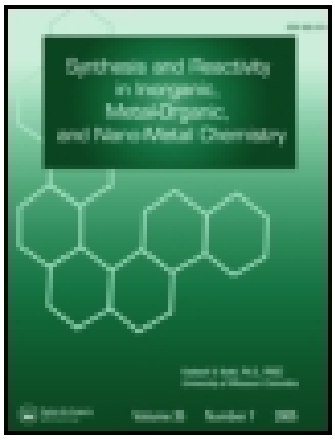

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$SbCl_5/SiO_2$ Nanoparticles: an efficient and reusable reagent for the synthesis of 4,4′-(Arylmethylene)bis(1H-pyrazol-5-ol) derivatives in water

Bahareh Sadeghi[a] & Maryam Ghorbani Rad[a]
[a] Department of Chemistry, Yazd Branch, Islamic Azad University, P.O. Box 89195-155, Yazd, Iran

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$SbCl_5/SiO_2$ Nanoparticles: an efficient and reusable reagent for the synthesis of 4,4´-(Arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives in water

Bahareh Sadeghi[1], Maryam Ghorbani Rad

Department of Chemistry, Yazd Branch, Islamic Azad University, P.O. Box 89195-155, Yazd, Iran

[1] Corresponding author. E-mail: bsadeghia@gmail.com

Abstract: An efficient and eco-friendly method for the synthesis of 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives is described by tandem Knoevenagel-Michael reaction between aromatic aldehydes and 3–methyl-1-phenyl-2-pyrazoline-5-one in the presence of nanosilica supported antimony pentachlorid ($SbCl_5/SiO_2$ NPs) in water. This method provides several advantages such as environmental friendliness, shorter reaction time, waste free, simple workup and excellent yields.

Keywords $SbCl_5/SiO_2$ NPs, aromatic aldehydes, 3–methyl-1-phenyl-2-pyrazoline-5-one, water

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-ol) derivatives 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-ol) derivatives has been reported in the presence of some catalyst such as ceric ammonium nitrate [10], sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester [11], silica-bonded *N*-propyltriethylenetetramine [12], xanthan sulfuric acid [13], phosphomolybdic acid [14], silica-bonded S-sulfonic acid [15] and pyridine trifluoroacetate [16].

The use of solid acid have received considerable importance in organic synthesis [17,18] because of their ease of handling, enhanced reaction times, greater selectivity, simple workup, and recoverability of catalyst. Since, Antimony pentachloride is a liquid with a high specific gravity that fumes in air and reacts with the moisture to form HCl. The handling and the usability of $SbCl_5$ as a liquid form is laborious and the supported form is indeed preferable. Supported $SbCl_5$ on SiO_2 nanoparticles has been prepared and has been used effectively as a catalyst. Application of environmentally benign water and solid acid catalyst represents powerful green procedure. In this work, the application of solid phase acidic and reusable nano catalyst ($SbCl_5/SiO_2$ NPs) have investigated for synthesis of 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives.

EXPERIMENTAL

Material and instrumentation

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.

The dimensions of nano-SiO_2 were observed with SEM (Figure 1). The stable silicagel nanoparticles is prepared [19] and used for preparation of catalyst ($SbCl_5/SiO_2$ NPs).

FIG. 1.

Synthesis of antimony pentachlorid supported on silicagel nanoparticles

The reagent was prepared by stirring a mixture of $SbCl_5$ (0.7 ml) and 1 g of nanosilica gel in 5 ml of chloroform for 1 h at room temperature. The slurry was filtered and washed with chloroform. The obtained solid ($SbCl_5/SiO_2$ NPs) was dried at an ambient temperature for 2 h and then stored in a dry container. The dimensions of nanoparticles were observed with SEM (Figure 2). The size of parsticles are between 30-37 nm.

FIG. 2.

General procedure for the preparation of compounds 3a-l

A mixture of 3–methyl-1-phenyl-2-pyrazoline-5-one (2 mmol), aromatic aldehyde (1 mmol), $SbCl_5/SiO_2$ NPs (0.004 g) and H_2O (5mL) 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 recrystallised from hot ethanol to obtain the pure compound.

The selected spectral data:

4,4´-(Phenylmethylene)bis(3-methyl-1-phenyl-1Hpyrazol-5-ol) (**3a**)

Colorless powder, m.p. 171-172 ºC; IR (ν_{max}, cm^{-1}): 3412, 3045, 2910, 1610, 1573, 1405, 1277, 1015, 743; ^{1}H NMR (500MHz, $CDCl_3$): δ 2.27 (s, 6H, $2CH_3$), 4.91 (s, 1H, CH), 7.15 (m, 1H), 7.24 (m, 6H), 7.39 (t, 4H, *J*= 7.6 Hz), 7.67 (d, 4H, *J*= 7.6 Hz), 14.05 (br s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.0, 33.5, 121.5, 126.4, 127.8, 128.7, 129.5, 137.4, 142.5, 146.7.

RESULTS AND DISCUSSION

In continuation of previous research on the use of solid acids in organic synthesis [20-24], the synthesis of 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives have investigated by condensation of 3–methyl-1-phenyl-2-pyrazoline-5-one **1** and an aromatic aldehyde **2** in the presence of 0.004g $SbCl_5/SiO_2$ NPs catalyst.

SCH. 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. The efficiency of $SbCl_5/SiO_2$ nanoparticles is comparable with other catalysts such as ceric ammonium nitrate, sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester, silica-bonded *N*-propyltriethylenetetramine, xanthan sulfuric acid, phosphomolybdic acid and silica-bonded S-sulfonic acid. According to the obtained data, xanthan sulfuric acid and phosphomolybdic acid have more yields but xanthan sulfuric acid has been applied (0.08 g) more amount and phosphomolybdic has lasted longer (240 min). These results clearly show the advantages of our methodology over other protic or Lewis acid catalyzed 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives synthesis such as low consumption of catalyst, shorter reaction time and excellent yields (Table 1, entry1-8). In order to determine the optimum quantity of $SbCl_5/SiO_2$ NPs, model reaction was carried out at reflux in water condition (Table1, entry 9-11). $SbCl_5/SiO_2$ NPs (0.004g) gave an excellent yield in 20 min (Table1, entry 10). 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 10). An interesting feature of this method is that the reagent can be regenerated at the end of the reaction and can be used several times without losing its activity. To recover the catalyst, after completion of the reaction, the mixture was filtered and catalyst was washed with $CHCl_3$ and then dries the solid residue. This process repeated for three cycles and the yield of product **3a** did not change significantly (Table 1, entry 14, 15). XRD analysis of the fresh and recovered catalyst was taken. As it shows peaks for pure SiO_2 and $SbCl_5$ exist in

this pattern that proof antimony pentachloride is supported on nano silica gel (Figure 3 and 4)

.

FIG. 3.

FIG. 4.

TABLE 1

To study the scope of the reaction, a series of aromatic aldehydes and 3–methyl-1-phenyl-2-pyrazoline-5-one catalysed by $SbCl_5/SiO_2$ NPs were examined (Scheme 1). 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.

TABLE 2

All products are known and were identified by their melting points, IR spectroscopy and elemental analyses.

CONCLUSION

In summary, a facile and mild procedure for the synthesis of 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives have been developed by condensation reaction of aromatic aldehydes and 3–methyl-1-phenyl-2-pyrazoline-5-one using nanosilica supported antimony pentachlorid

($SbCl_5/SiO_2$ NPs) as an efficient, eco-friendly and reusable heterogeneous catalyst. The main advantages of the present synthetic protocol are mild, high yields, short reaction times and easy reaction work up procedure.

ACKNOWLEDGEMENTS

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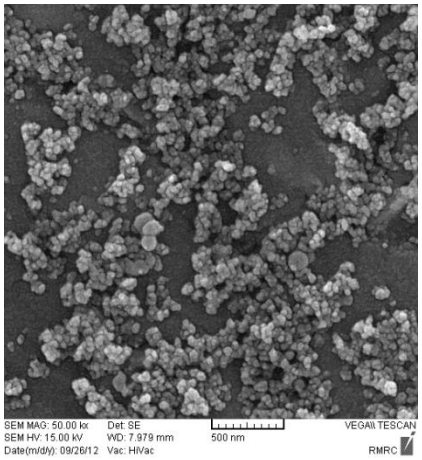


FIG. 1. The SEM images of SiO_2 nanoparticles

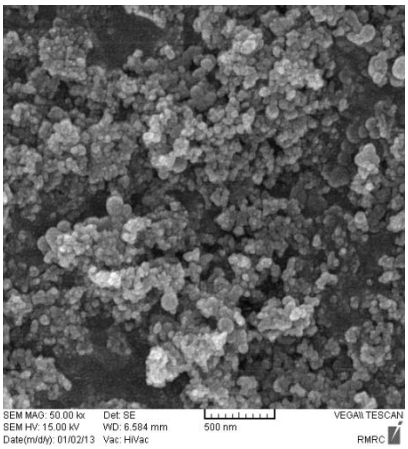


FIG. 2. The SEM images of $SbCl_5/SiO_2$ NPs

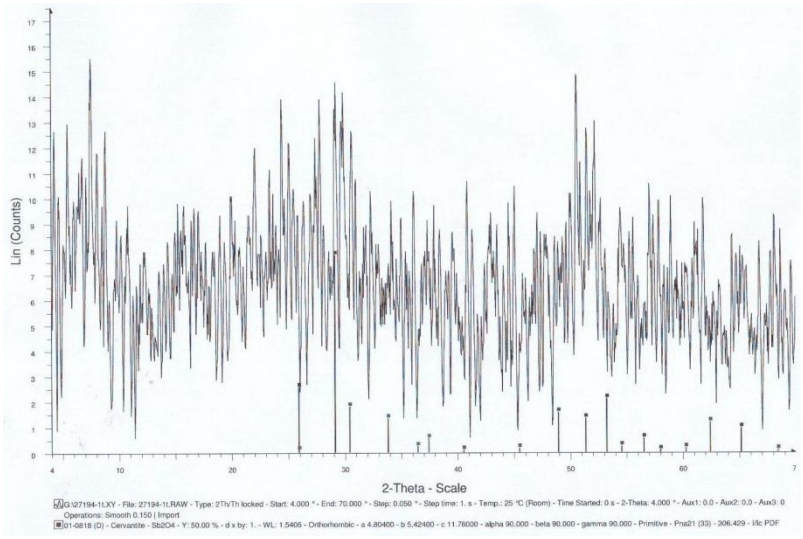


Fig. 3. The XRD pattern of $SbCl_5/SiO_2$ NPs

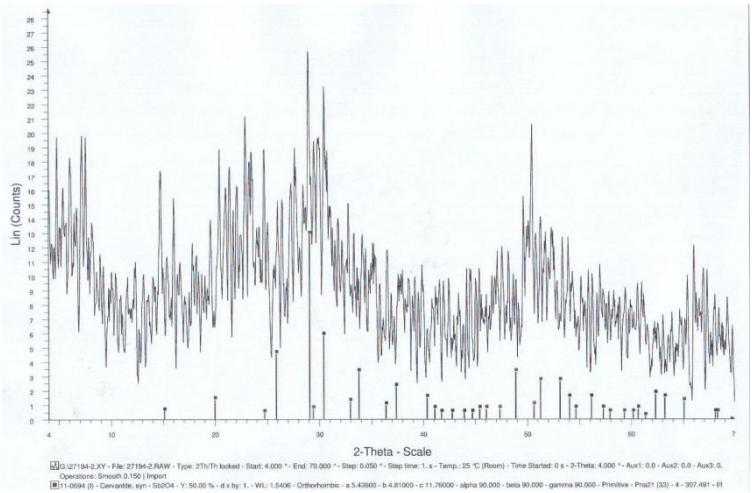
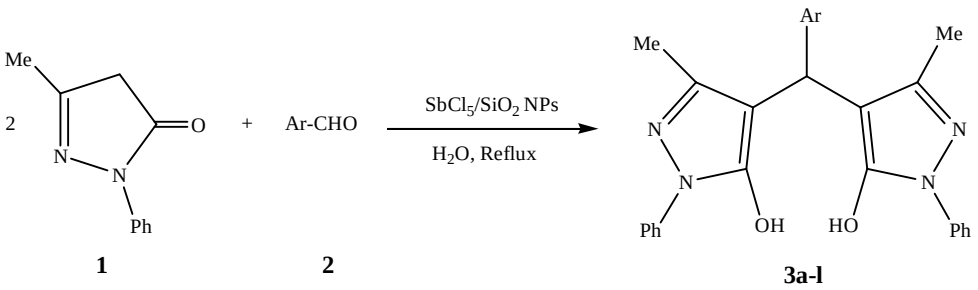


Fig. 4. The XRD pattern of recovered $SbCl_5/SiO_2$ NPs



1 **2** **3a-l**

SCH. 1. The condensation of aromatic aldehydes with 3–methyl-1-phenyl-2-pyrazoline-5-one using $SbCl_5/SiO_2$ NPs as catalyst

TABLE 1 Comparison of the efficiency of $SbCl_5/SiO_2$ NPs with reported catalysts for the synthesis of **3a** and optimization of the reaction condition

Entry	Catalyst (amount)	Cond./Sol.	Time (min)	Yield[a](%)	Ref.
1	Ceric ammonium nitrate (5 mol%)	25 ºC/H_2O	15	92	10
2	SASPSPE[b] (0.1 g)	80 ºC/EtOH	180	90	11
3	SBNPTT [c] (0.03 g)	80 ºC/EtOH	30	90	12
4	Xanthan sulfuric acid (0.08 g)	80 ºC/EtOH	15	95	13
5	Phosphomolybdic acid (1 mol%)	25 ºC/EtOH	240	96	14
6	SBSSA [d] (0.1 g)	80 ºC/EtOH	120	80	15
7	$SnCl_4/SiO_2$ NPs(0.004 g)	100 ºC/ H_2O	20	84	-
8	BF_3/SiO_2 NPs (0.004 g)	100 ºC/H_2O	20	82	-
9	$SbCl_5/SiO_2$ NPs (0.002 g)	100 ºC/H_2O	20	85	-
10	$SbCl_5/SiO_2$ NPs (0.004 g)	100 ºC/H_2O	20	95	-
11	$SbCl_5/SiO_2$ NPs (0.006 g)	100 ºC/H_2O	20	96	-
12	$SbCl_5/SiO_2$ NPs (0.004 g)	80 ºC/EtOH	20	87	-
13	$SbCl_5/SiO_2$ NPs (0.004 g)	40 ºC/CH_2Cl_2	20	83	-
14	$SbCl_5/SiO_2$ NPs (0.004 g) 2^{nd} run	100 ºC/H_2O	20	88	-
15	$SbCl_5/SiO_2$ NPs (0.004 g) 3^{nd} run	100 ºC/H_2O	20	82	-

[a]Isolated yield, [b] Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester, [c] Silica-bonded *N*-propyltriethylenetetramine, [d] Silica-bonded S-sulfonic acid,

TABLE 2

$SbCl_5/SiO_2$ NPs catalyzed the synthesis of 4,4´-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives

Entry	Ar	Product	Yield[a]%	m.p./ºC	
				Found	Reported[Ref]
1	C_6H_5	3a	95	171-172	170-171[10]
2	2-BrC_6H_4	3b	87	199-200	198-200[11]
3	4-FC_6H_4	3c	90	182-184	181-183[11]
4	4-MeC_6H_4	3d	92	203-205	203-204[10]
5	2-OHC_6H_4	3e	88	229-230	227-229[11]
6	4-CNC_6H_4	3f	92	208-210	210-212[11]
7	3-$NO_2C_6H_4$	3g	93	152-153	151-153[11]
8	4-$NO_2C_6H_4$	3h	96	224-226	225-227[11]
9	2-ClC_6H_4	3i	84	236-237	235-237[11]
10	4-ClC_6H_4	3j	91	217-218	215-217[11]
11	2-Furfuryl	3k	93	189-191	189-190[10]
12	2-Pyridyl	3l	92	230-232	232-233[10]

[a]Isolated yield.