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SbCl₅/SiO₂ Nanoparticles: an efficient and reusable reagent for the synthesis of 4,4'- (AryImethylene)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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SbCl₅/SiO₂ Nanoparticles: an efficient and reusable reagent for the synthesis of 4,4'-

(Arylmethylene)bis(1H-pyrazol-5-ol) derivatives in water

Bahareh Sadeghi¹, Maryam Ghorbani Rad

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

Iran

¹ Corresponding author. E-mail: <u>bsadeghia@gmail.com</u>

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 (SbCl₅/SiO₂ NPs) in water. This method provides several advantages such as environmental friendliness, shorter reaction time, waste free, simple workup and excellent yields.

Keywords SbCl₅/SiO₂ 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 SbCl₅ as a liquid form is laborious and the supported form is indeed preferable. Supported SbCl₅ on SiO₂ 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 (SbCl₅/SiO₂ 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-SiO₂ were observed with SEM (Figure 1). The stable silicagel nanoparticles is prepared ^[19] and used for preparation of catalyst (SbCl₅/SiO₂ 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.

³ ACCEPTED MANUSCRIPT

General procedure for the preparation of compounds 3a-1

A mixture of 3-methyl-1-phenyl-2-pyrazoline-5-one (2 mmol), aromatic aldehyde (1 mmol), SbCl₅/SiO₂ NPs (0.004 g) and H₂O (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 °C; IR (v_{max} , cm⁻¹): 3412, 3045, 2910, 1610, 1573, 1405, 1277, 1015, 743; ¹H NMR (500MHz, CDCl₃): δ 2.27 (s, 6H, 2CH₃), 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; ¹³C NMR (125 MHz, CDCl₃): 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 SbCl₅/SiO₂ 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-(3silicapropyl)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(1H-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 SbCl₅/SiO₂ NPs, model reaction was carried out at reflux in water condition (Table1, entry 9-11). SbCl₅/SiO₂ 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 CHCl₃ 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-2pyrazoline-5-one catalysed by SbCl₅/SiO₂ 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

(SbCl₅/SiO₂ 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.

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FIG. 1. The SEM images of SiO₂ nanoparticles

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FIG. 2. The SEM images of SbCl₅/SiO₂ NPs

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Fig. 3. The XRD pattern of SbCl₅/SiO₂ NPs



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



SCH. 1. The condensation of aromatic aldehydes with 3-methyl-1-phenyl-2-pyrazoline-5-one using SbCl₅/SiO₂ 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	Yield ^a (%)	Ref.
			(min)		
1	Ceric ammonium nitrate (5 mol%)	25 °C/H ₂ O	15	92	10
2	SASPSPE ^b (0.1 g)	80 °C/EtOH	180	90	11
3	SBNPTT ^c (0.03 g)	80 °C/EtOH	30	90	12
4	Xanthan sulfuric acid (0.08 g)	80 °C/EtOH	15	95	13
5	Phosphomolybdic acid (1 mol%)	25 °C/EtOH	240	96	14
6	SBSSA ^d (0.1 g)	80 °C/EtOH	120	80	15
7	SnCl ₄ /SiO ₂ NPs(0.004 g)	100 °C/ H ₂ O	20	84	-
8	BF ₃ /SiO ₂ NPs (0.004 g)	100 °C/H ₂ O	20	82	-
9	SbCl ₅ /SiO ₂ NPs (0.002 g)	100 °C/H ₂ O	20	85	-
10	SbCl ₅ /SiO ₂ NPs (0.004 g)	100 °C/H ₂ O	20	95	-
11	SbCl ₅ /SiO ₂ NPs (0.006 g)	100 °C/H ₂ O	20	96	-
12	SbCl ₅ /SiO ₂ NPs (0.004 g)	80 °C/EtOH	20	87	-
13	SbCl ₅ /SiO ₂ NPs (0.004 g)	40 °C/CH ₂ Cl ₂	20	83	-
14	SbCl ₅ /SiO ₂ NPs (0.004 g) 2 nd run	100 °C/H ₂ O	20	88	-
15	SbCl ₅ /SiO ₂ NPs (0.004 g) 3 nd run	100 °C/H ₂ O	20	82	-

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

TABLE 2

SbCl₅/SiO₂ NPs catalyzed the synthesis of 4,4⁻-(arylmethylene)bis(1H-pyrazol-5-ol) derivatives

Ar	Product	Yield ^a %	m.p./°C	
			Found Reported ^[Ref]	
C_6H_5	3a	95	171-172	170-171 ^[10]
$2-BrC_6H_4$	3b	87	199-200	198-200 ^[11]
$4-FC_6H_4$	3c	90	182-184	181-183 ^[11]
$4-MeC_6H_4$	3d	92	203-205	203-204 ^[10]
2-OHC ₆ H ₄	3e	88	229-230	227-229 ^[11]
4-CNC ₆ H ₄	3f	92	208-210	210-212 ^[11]
$3-NO_2C_6H_4$	3g	93	152-153	151-153 ^[11]
$4-NO_2C_6H_4$	3h	96	224-226	225-227 ^[11]
$2-ClC_6H_4$	3i	84	236-237	235-237 ^[11]
$4-ClC_6H_4$	3ј	91	217-218	215-217 ^[11]
2-Furfuryl	3k	93	189-191	189-190 ^[10]
2-Pyridyl	31	92	230-232	232-233 ^[10]
	Ar C_6H_5 $2-BrC_6H_4$ $4-FC_6H_4$ $4-MeC_6H_4$ $2-OHC_6H_4$ $4-CNC_6H_4$ $3-NO_2C_6H_4$ $4-NO_2C_6H_4$ $4-CIC_6H_4$ $4-CIC_6H_4$ $2-Furfuryl$ $2-Pyridyl$	ArProduct C_6H_5 3a 2 -BrC ₆ H ₄ 3b 4 -FC ₆ H ₄ 3c 4 -FC ₆ H ₄ 3d 2 -OHC ₆ H ₄ 3d 2 -OHC ₆ H ₄ 3f 3 -NO ₂ C ₆ H ₄ 3g 4 -NO ₂ C ₆ H ₄ 3h 2 -CIC ₆ H ₄ 3i 4 -CIC ₆ H ₄ 3j 2 -Furfuryl3k 2 -Pyridyl31	ArProductYield ^a % C_6H_5 $3a$ 95 2 -Br C_6H_4 $3b$ 87 4 -F C_6H_4 $3c$ 90 4 -Me C_6H_4 $3d$ 92 2 -OH C_6H_4 $3e$ 88 4 -CN C_6H_4 $3f$ 92 3 -NO $_2C_6H_4$ $3g$ 93 4 -NO $_2C_6H_4$ $3h$ 96 2 -CI C_6H_4 $3i$ 84 4 -CI C_6H_4 $3j$ 91 2 -Furfuryl $3k$ 93 2 -Pyridyl $3l$ 92	ArProductYield ^a %m C_6H_5 3a95171-1722-BrC_6H_43b87199-2004-FC_6H_43c90182-1844-MeC_6H_43d92203-2052-OHC_6H_43e88229-2304-CNC_6H_43f92208-2103-NO_2C_6H_43g93152-1534-NO_2C_6H_43h96224-2262-CIC_6H_43i84236-2374-CIC_6H_43j91217-2182-Furfuryl3k93189-1912-Pyridyl3192230-232

^aIsolated yield.

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