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ARTICLE

1,3,5-Tris(hydrogensulfato) Benzene: A New and Efficient Catalyst for Synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) Derivatives

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Abstract: 1,3,5-Tris(hydrogensulfato) benzene (THSB) was easily prepared by the reaction between phloroglucinol and chlorosulfonic acid in dichloromethane at room temperature. This compound was then used as an efficient catalyst for the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ols) through the condensation reactions of 1-phenyl-3-methylpyrazol-5-one with several different aromatic aldehydes in ethanol at 75 °C. The present methodology offers several advantages over existing methodologies, such as excellent yields, simple procedure, easy work-up and ecofriendly reaction conditions.

Key words: 1,3,5-tris(hydrogensulfato) benzene; aromatic aldehydes; 1-phenyl-3-methylpyrazol-5-one; 4,4'-(arylmethylene)bis (1*H*-pyrazol-5-ols); ethanol; multicomponent reaction

Heterocycles represent the largest of the classical divisions in organic chemistry by far and are of immense importance both biologically and industrially. Pyrazoles are an important class of heterocyclic compound. Examination of the chemical literature reveals that a great many synthetic pyrazole derivatives have been reported, with applications across a wide range of fields, where they have been used as pharmaceuticals, agrochemicals, and photographic agents. 2,4-Dihydro-3H-pyrazol-3-one derivatives, including the 4,4'-(arylmethylene) bis(1*H*-pyrazol-5-ols) have a broad spectrum of approved biological activity, and have been used as anti-inflammatory [1], antipyretic [2], gastric secretion stimulatory [3], antidepressant [4], antibacterial [5], antiviral [6], and antifilarial agents [7]. They have also used as fungicides [8], insecticides [9], and dyestuffs [10–13].

Over the years, multicomponent reactions [14–16] (MCRs) have become increasingly popular as tools for enabling the introduction of sufficient molecular diversity and complexity. These reactions have gained significant popularity in recent years because of their atom-economy and straightforward reaction design, which also allows for substantial minimization in the levels of waste generated from the process with considerable saving in labor, time, and costs [17–19]. MCRs leading to the generation of interesting heterocyclic scaffolds are particularly useful for the construction of diverse chemical libraries of 'drug like' molecules.

Recently, several different three component one-pot condensation reactions have been reported between 1-phenyl-3-methylpyrazol-5-one and a variety of different aldehydes for the construction of 4,4'-(arylmethylene)bis (1*H*-pyrazol-5-ol) derivatives [6, 20–32]. Several different catalysts have been reported to promote this reaction, including ceric ammonium nitrate (CAN) [6], sodium dodecyl sulfate (SDS) as a surfactant catalyst [20], ETBA [21], NaBr [22], $[Cu(3,4\text{-tmtppa})](MeSO_4)_4$ [23], silica-bonded S-sulfonic acid (SBSSA) [24], silica sulfuric acid (SSA) [25], H_2O [26], sulfuric acid ([3-(3-silicapropyl)sulfanyl] propyl)ester (SASPSPE) [27], xanthan sulfuric acid [28], PEG-SO_3H [29], ionic liquid [HMIM]HSO_4 [30], 3-minopropylated silica gel (AP-SiO_2) [31], and phosphomolybdic acid [32].

Although some of these methods afford moderate to high yields of the corresponding products, the majority suffer from one or more of the following disadvantages, including (1) the use of a costly catalyst; (2) the requirement for a tedious work-up procedure; (3) the need for high temperatures; and (4) long reaction times. Herein, we report the development of a

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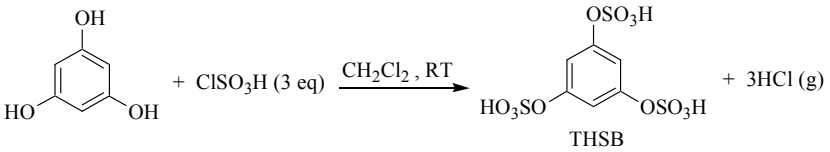


Scheme 1. Preparation of THSB.

mild, efficient, and environmentally benign procedure for the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivates from the condensation reaction of aldehydes and 1-phenyl-3-methylpyrazol-5-one in the presence of 1,3,5-tris(hydrogensulfato) benzene (THSB) as an efficient and new catalyst.

1 Experimental

1.1 General

All of the chemicals were purchased from Merck and Aldrich. Melting points were determined in open capillary tubes and are uncorrected. IR measurements were carried out using KBr pellets on a Fourier transform infrared (FT-IR) spectrometer (Manufacturer, City, State/Country). ^{1}H (250 MHz) and ^{13}C (62.5 MHz) NMR spectra were recorded on a Bruker Avance 250 spectrometer (Bruker, City, State/Country) in DMSO-d_6 using tetramethylsilane (TMS) as an internal reference. All of the products have been reported previously in the literature and were characterized according to their spectral and physical data. Reaction monitoring for the progress of all of the reactions was carried out by thin-layer chromatography (TLC) using silica gel 60 GF_{245} precoated sheets and were visualized using a UV-lamp at a wave length of 254 nm. All chemicals and solvents were of reagent grade and the latter were distilled and dried before use. The elemental analyses were performed with an Elementar Analysensysteme GmbH VarioEL in CHNS mode.

1.2 Preparation of THSB

A solution of chlorosulfonic acid (8.74 g, ca. 5 ml, 75 mmol) in CH_2Cl_2 (20 ml) was added to phloroglucinol (3.15 g, 25 mmol) in a drop-wise manner over a period of 1 h at room temperature (Scheme 1). HCl evolved immediately. Upon completion of the addition, the mixture was shaken for 3 h, and the residual HCl was removed by suction. The solid residue was washed with *n*-hexane (10 ml) and filtered to give the desired product as a yellow solid material in 95% yield.

1.3 General procedure for the one-pot synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives

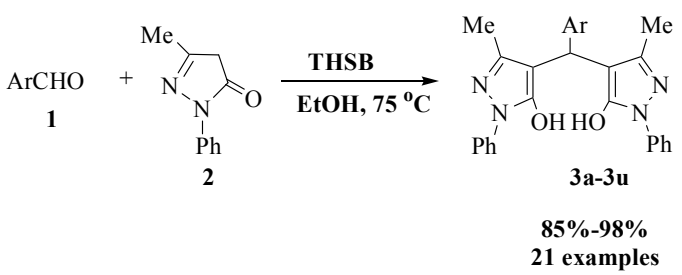
THSB (0.04 mmol, 0.014 g) and silica gel (0.006 g) were added to a solution of aromatic aldehyde **1** (1 mmol, Scheme 2) and 1-phenyl-3-methylpyrazol-5-one **2** (2 mmol, scheme 2) in ethanol (2 ml), and the resulting mixture was stirred at 75 °C for the specified period of time, as indicated in Table 1. Upon completion of the reaction, as confirmed by TLC, the reaction mixture was cooled to room temperature. The resulting precipitated product was then filtered and washed with *n*-hexane (10 ml) to afford the pure product **3** (**3a**–**3u**) as a white powder.

1.4 Characterization of some representative compounds

THSB. Pale yellow solid. IR (KBr, cm^{-1}): 3403, 1284, 1174, 578. ^{1}H NMR (250 MHz, DMSO-d_6): 5.82 (s, 3H, ArH). Anal. Calcd For $C_6H_6O_{12}S_3$: C, 19.67; H, 1.65; S, 26.26; Found: C, 19.57; H, 1.59; S, 26.19.

4,4'-[(4-Chloro-3-nitrophenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 1, Entry 10, **3j**). Pale yellow solid. IR (KBr, cm^{-1}): 3425, 3054, 2923, 1598, 1570, 1530, 1501, 1368, 750. ^{1}H NMR (250 MHz, DMSO-d_6): 2.32 (s, 6H, 2CH_3), 5.80 (s, 1H, CH), 7.23 (d, 2H, J = 2.5 Hz, ArH), 7.25 (d, 4H, J = 2.5 Hz, ArH), 7.54–7.57 (m, 1H, ArH), 7.65–7.66 (m, 5H, ArH), 7.84 (s, 1H, ArH); ^{13}C NMR (62.5 MHz, DMSO-d_6): 11.9, 104.1, 121.1, 122.9, 124.6, 126.2, 129.1, 129.4, 131.7, 133.3, 137.4, 144.0, 146.7, 147.8. Anal. Calcd For $C_{27}H_{22}C_lN_5O_4$: C, 62.85; H, 4.30; N, 13.57; Found: C, 62.74; H, 4.25; N, 13.50.

4,4'-[(2-Methoxyphenyl)methylene]bis(3-methyl-1-phenyl-



Scheme 2. Synthesis of the 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives catalyzed by THSB.