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$Al(HSO_4)_3$/silica gel as a novel catalytic system for the ring opening of epoxides with thiocyanate anion under solvent-free conditions

Ali Reza Kiasat *, Arash Mouradzadegun, Somayeh Elahi, Mehdi Fallah-Mehrjardi

Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran

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Abstract

For the first time, metal hydrogen sulfates and phosphates/silica gel have been studied as efficient and powerful solid acid catalysts in the ring opening of epoxides with thiocyanate anion. The most significant result was obtained by $Al(HSO_4)_3/SiO_2$ which afforded the corresponding β-hydroxy thiocyanates under mild reaction conditions and in very short reaction times. The cheapness, availability of the catalyst, ease of procedure and work-up make this method attractive for the organic synthesis.

Keywords: Metal hydrogen sulfates; Solid acid catalysts; Ring opening of epoxides; β-Hydroxy thiocyanates

Acid catalysts are of fundamental importance because of their ubiquity [1]. In view of green chemistry, the substitution of harmful liquid acids by reusable solid acids as catalysts in organic synthesis is the most promising application [2]. Recently, solid acids as environmentally friendly and economically viable catalyst, are increasing continuously owing to their ease of handling, low cost, high catalytic activity, process simplicity and comparably easy work-up [3]. In addition, solid acids, in many cases, show better selectivity than mineral acids toward a specific isomer in a mixture of reaction products [4]. Finally, supported solid acid provides more effective catalytic reactivity by their much extended surface area [5].

The development of versatile and efficient methods for the synthesis of β-hydroxy thiocyanates continues to be an active area of research, because they play an important role in the realm of organic chemistry, such as biological, pharmaceutical and agricultural chemistry [6]. From a fundamental viewpoint, ring opening of epoxides by thiocyanate anion is a well-established route to thiiranes, achieved commonly through the corresponding β-hydroxy thiocyanates as intermediates [7,8]. It has been reported that a portion of hydroquinone [9] or DDQ [6] is required to stabilize the produced β-hydroxy thiocyanate, and to inhibit conversion to the respective thiirane. Although a few useful reagents reported for the ring opening of epoxide to the thiocyanohydrin [10–14], however, to the best of our knowledge, there have been no previous studies on the use of metal hydrogen sulfates ($M(HSO_4)_n$) and metal dihydrogen phosphates ($M(H_2PO_4)_n$) as effective catalysts for regioselective ring opening of epoxides in the literature.

Looking for ‘‘cleaner’’ alternatives to classical syntheses [7,15] and in developing green chemistry [16–18] and also in pursuing our new interest in developing inexpensive and non polluting reagents [18–21], we report herein

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* Corresponding author.
E-mail address: akiasat@scu.ac.ir (A.R. Kiasat).

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studies of $M(HSO_4)_n/SiO_2$ and $M(H_2PO_4)_n/SiO_2$ as efficient catalysts for the ring opening of epoxides with thiocyanate anion at room temperature under solvent-free conditions.

1. Experimental

1.1. Preparation of metal hydrogen sulfates and phosphates supported on silica gel

A 50 mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. Anhydrous metal chlorides (10 mmol) were charged in the flask and appropriate amount of concentrated sulfuric acid or phosphoric acid (20 mmol for $MgCl_2$ and $ZnCl_2$ and 30 mmol for $AlCl_3$) was added dropwise over a period of 45 min at room temperature. HCl evolved immediately. After completion of the addition, the mixture was shaken for 30 min, while the residual HCl was eliminated by suction. Finally, the obtained pale-brown solid materials were ground with silica gel (weight ratio of silica gel to obtained catalyst was 2:1) in an agate mortar to form an intimate mixture.

1.2. Typical procedure for the preparation of β-hydroxy thiocyanates catalyzed by $Al(HSO_4)_3/SiO_2$ under solvent-free conditions

A mortar was charged with epoxide (1 mmol), NH_4SCN (1.2 mmol) and $Al(HSO_4)_3/SiO_2$ (0.3 mmol base on catalyst). The mixture was ground with a pestle until the TLC assay showed complete disappearance of the starting material. On completion of the reaction, the reaction mixture was poured into ethyl acetate (10 mL) and filtered to remove the solids. The solid residue was then washed with ethyl acetate (5 mL) and the filtrate washed with water (20 mL). The organic layer was dried over anhydrous sodium sulfate and solvent evaporated under reduced pressure to give the corresponding β-hydroxy thiocyanates in excellent isolated yields. For styrene oxide, further purification was achieved by preparative TLC or by silica gel column chromatography.

2. Results and discussion

Metal hydrogen sulfates and phosphates were easily prepared from the corresponding anhydrous metal chlorides and sulfuric or phosphoric acid, respectively [22,23]. The reactions are very clean and did not require a work-up procedure because HCl evolves as a by-product from the reaction vessel immediately (Scheme 1).

Initially we attempt to investigate the possible catalytic properties of these solid acids (I–VI) with simpler systems such as phenyl glycidyl ether (1 mmol) with NH_4SCN (2 mmol). Under solvent-free conditions, comparative results led us to introduce $Al(HSO_4)_3/SiO_2$ as the most effective system (Table 1).

Encouraged by this observation, further experiments were designed to optimizing this conversion in the presence of $Al(HSO_4)_3/SiO_2$. To determine the relative molar ratio of reactants and catalyst we arranged a systematic experiment. The best results were obtained when 0.3 mmol of catalyst and 1.2 mmol of reactant were used (Table 2).

The effect of the solvent on the performance of promoted catalyst was also investigated (Table 3). The results clearly revealed that, although ethyl acetate and acetonitrile represented a good compromise in reflux conditions, yet the best results were obtained under solvent-free conditions.

The generality of this process was explored with respect to various epoxides (Table 4). In all cases, very clean reactions were observed and the structure of all the products was determined from spectral assignments (IR, ^1H and ^{13}C NMR) through comparisons with data from authentic samples [18]. As shown in Table 4, cyclohexene oxide as a cycloalkyl epoxide reacted smoothly in a S_N2 fashion with NH_4SCN in the presence of catalytic amount of

$$MCl_n + n\,H_2SO_4 \longrightarrow M(HSO_4)n + n\,HCl$$

$$MCl_n + n\,H_3PO_4 \longrightarrow M(H_2PO_4)n + n\,HCl$$

Cat I : $Al(HSO_4)_3$; Cat II : $Mg(HSO_4)_2$; Cat III : $Zn(HSO_4)_2$;
Cat IV : $Al(H_2PO_4)_3$; Cat V : $Mg(H_2PO_4)_2$; Cat VI : $Zn(H_2PO_4)_2$

Scheme 1.