

A green method for the synthesis of β -hydroxy thiocyanates in water

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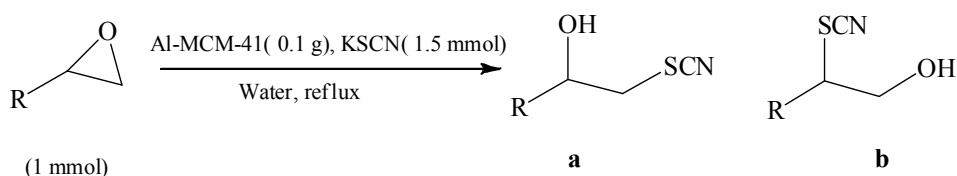
Abstract. An efficient and green procedure has been developed for the synthesis of β -hydroxy thiocyanate by the regioselective ring opening of epoxides with KSCN. The reaction was carried out in water without any organic solvent in 40 °C, using nanosized Al-MCM-41 (a mesoporous aluminosilicat) as catalyst. In this method, several types of epoxides carrying electron-donating or with-drawing groups were rapidly converted to the corresponding β -hydroxy thiocyanates in good to excellent yields. Various advantages associated with this protocol include simple workup procedure, short reaction times, high product yields, greater regioselectivity and easy recovery and reusability of the catalyst.

Keywords: Al-MCM-41; Ring opening reaction; β -hydroxy thiocyanates

1. Introduction

Chemical processes employ large amounts of hazardous and toxic solvents. One of the challenges for the chemists is to come up with new approaches that are less hazardous to human and environment. The choice of pursuing a low waste route and reusable reaction media, and minimize the economic cost and environmental impact of a chemical process, are becoming ever more urgent for the future. One of the most promising approaches uses water as reaction medium. Water is an abundant, cheap, non-toxic, and non-dangerous solvent.¹

From green chemistry point of view, there is an increasing demand for transformation of homogeneous into heterogeneous catalysis in organic synthesis, especially in fine chemicals synthesis due to the ease with which catalysts can be separated from products and recycled.² Micro- and mesoporous materials offer unique opportunities for heterogeneous catalysis by their large surface area. Recently; a wide range of acid–base or redox catalysts has been developed by modification of such material via introducing active elements inside the pore walls.^{3, 4} Mesoporous aluminosilicate, Al-MCM-41, is well known to show remarkable acidic properties. Since its pore sizes are larger than those of zeolites, bulky organic substrates can contact acid sites of mesoporous aluminosilicates.⁵ Therefore, Al-MCM-41 molecular sieves have been shown to catalyze several organic transformations. However, most of these reactions are vapor phase or high-temperature reactions, and there has been relatively few reports on the synthetic application of Al-MCM-41 as a solid acid catalyst for liquid-phase reactions under mild reaction conditions.⁶ Because of the importance of β -hydroxy thiocyanates in the field of synthetic organic chemistry⁸ and in continuation of our ongoing effort to introduce novel catalysts for organic transformation,⁹⁻¹³ in this project we decided to explore the use of nanosized Al-MCM-41 as an efficient catalyst for the synthesis of β -hydroxy thiocyanates by the regioselective ring opening of epoxides under mild and eco-friendly conditions (Scheme 1).

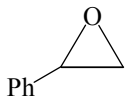
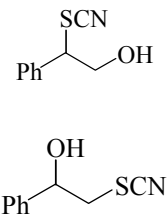
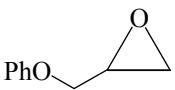
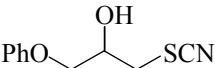
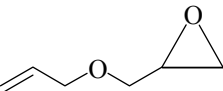
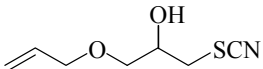
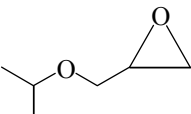
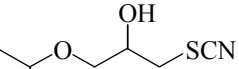
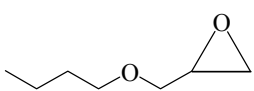
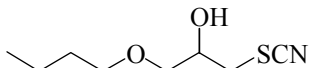
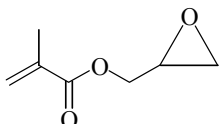
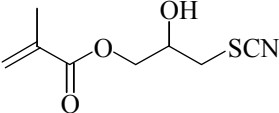
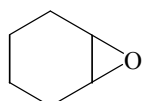
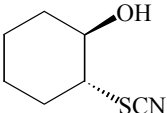


Scheme 1

2. Results and discussion

First, the Al-MCM-41 nanoreactors were prepared in our laboratory according to the reported method.¹⁴ Then, the Al-MCM-41-catalyzed ring opening of epoxide, was applied to synthesis of various β -hydroxy thiocyanates in the presence of thiocyanate anion. Under optimized reaction conditions several types of epoxides carrying electron-donating or with-drawing groups were rapidly converted to the corresponding product in good to excellent yields in aqueous media at 40 °c. The results are summarized in Table 1.

Table 1.

| Entry | Epoxide | Product ^a | Time (min) | Yield ^b (%) |
|-------|---|---|------------|------------------------|
| 1 |  |  | 15 | 87 |
| 2 |  |  | 30 | 90 |
| 3 |  |  | 15 | 83 |
| 4 |  |  | 15 | 85 |
| 5 |  |  | 15 | 80 |
| 6 |  |  | 15 | 82 |
| 7 |  |  | 25 | 80 |

[1] ^a Products were identified by comparison of their physical and spectral data with those of authentic samples.

[2] ^b Isolated yields.

In all cases, very clean reactions were observed and the structures and the regiochemical ratios of products were determined by FT-IR, ¹H NMR and ¹³C NMR spectroscopy and also by comparison with authentic compounds. It is also worth mentioning that the Al-MCM-41 catalyst was easily recovered by simple filtration, and showed no appreciable loss of activity and without any variation in the reaction times or the yields of the corresponding products when recycled several times.

Table 2.

| Entry | Catalyst | Time(min) | Yield (%) |
|-------|-------------------------------------|-----------|-----------|
| 1 | Selectfluor ¹⁵ | 150 | 95 |
| 2 | Ti(O ⁱ Pr) ¹⁶ | 240 | 30 |
| 3 | PEG-SO ₃ H ¹⁷ | 60 | 84 |
| 4 | PPI ¹⁸ | 45 | 95 |
| 5 | PTC ¹⁹ | 90 | 90 |
| 6 | CoT(4-OH)P ²⁰ | 25 | 96 |

The regioselectivity and advantages of Al-MCM-41 catalyst were highlighted by comparison of conversion of styrene oxide to β -hydroxy thiocyanates with those of reported in literature (Table 2). A case study shows that in view points of reusability of the catalyst, short reaction times, perfect regioselectivity and efficiency, our protocol is more efficient than the others.

3. Experimental Section

3.1. General comments

Products were characterized by comparison of their physical data, IR and ¹H NMR spectra with known samples. NMR spectra were recorded in CDCl₃ on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer.

3.2. Typical procedure for the preparation of β -hydroxy thiocyanates catalyzed by Al-MCM-41

To a suspension of Al-MCM-41 (100 mg), which was pretreated in vacuo at 120 °C for 1 h, KSCN (145 mg, 1.5 mmol) in water (5 mL) was added epoxide (1.0 mmol). The mixture was magnetically stirred at 40 °C for the time shown in Table 1. After complete consumption of epoxide as judged by TLC (using *n*-hexane/ethylacetate (5:1) as eluent), the insoluble Al-MCM-41 catalyst was filtered off and the filtrate was extracted with ether (3 × 5). The extract was dried over Na₂SO₄, and evaporated in vacuo to give the alcohols. The crude products were purified by silica gel column chromatography.

4. Acknowledgments

The authors gratefully acknowledge the funding support received for this project from Islamic Azad University, Mahshahr Branch Research Council.

5. Reference

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