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NOTE

Sulfuric Acid Impregnated on Silica Gel (H_2SO_4/SiO_2): A Versatile and Reusable Catalyst for the Synthesis of 1,2,4-Triazolo[5,1-b][1,3]thiazin-7-ones

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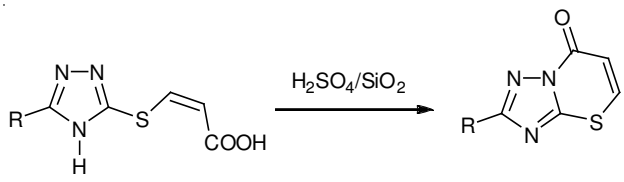
Sulfuric acid adsorbed on silica gel (H_2SO_4/SiO_2) has been found to be a highly efficient and versatile catalyst for the cyclization of 3-(4*H*-1,2,4-triazol-3-ylsulfanyl)-acrylic acids into 1,2,4-triazolo[5,1-b][1,3]-thiazin-7-ones under solvent-free microwave irradiation and conventional heating. The present methodology offers several advantages such as simple procedure with an easy work-up, short reaction times, high yields and a recyclable, relatively green and eco-friendly catalyst.

Key Words: Triazolothiazine, H_2SO_4/SiO_2, Microwave irradiation, Solvent-free conditions.

Solid-supported catalysts have found tremendous popularity in several disciplines of chemistry. These catalysts are recyclable, efficient, green and eco-friendly[1-5]. In recent years it has been shown that sulfuric acid adsorbed on silica gel can be used as a multipurpose acid catalyst[6-8]. In previous paper, a new route to the synthesis of 1,2,4-triazolo[5,1-b][1,3]thiazin-7-ones through cyclization of 3-(4*H*-1,2,4-triazol-3-yl- sulfanyl)acrylic acids using conc. H_2SO_4 at 50 ºC has been reported[9]. H_2SO_4 is an environmentally harmful liquid acid catalyst and work-up procedures are difficult in the presence of this catalyst.

Prompted by these findings and interest in utilization of microwave irradiation for the synthesis of heterocyclic compounds[10-15], in this paper an efficient method for transformation of 3-(4*H*-1,2,4-triazol-3-ylsulfanyl)-acrylic acids **(1a-c)** to 1,2,4-triazolo[5,1-b][1,3]thiazin-7-ones **(2a-c)** using sulfuric acid adsorbed on silica gel as an efficient, green and eco-friendly catalyst under solvent-free microwave irradiation and conventional heating is reported (**Scheme-I**).

Melting points were recorded on an electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrophotometer as KBr disks. The ^{1}H NMR (100 MHz) spectra were recorded on a Bruker AC 100 spectrometer. All products were known and characterized by comparison of their physical and spectroscopic data with those of already reported[9].



1a-c **2a-c**

Scheme-I

Preparation of the catalyst H_2SO_4/SiO_2: A solution of conc. H_2SO_4 (2 mL) in acetone (20 mL) is added to a dispersion of silica gel 60 (70-230 mesh) (100 g) in acetone (200 mL) and stirred at room temperature for 1 h. The solvent is removed under reduced pressure. A yellow-brown powder is obtained, which can be stored in a desicator for long periods of times without any appreciable loss of activity.

General procedure for the preparation of 1,2,4-triazolo[5,1-b][1,3]thiazin-7-ones (2a-c)

Method A: A mixture of 3-(4*H*-1,2,4-triazol-3-ylsulfanyl)-acrylic acids **1a-c** (2 mmol) and H_2SO_4/silica gel (0.6 g) was subjected to microwave irradiation at 700 w for the indicated time. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature and boiling ethanol was added. The catalyst was filtrated and the filtrate was concentrated to give the solid product that was recrystallized from ethanol/water to give compounds **2a-c** in 70, 73 and 80 % yields, respectively (Table-1, **method A**).

TABLE-1
COMPARISON OF TIME AND YIELDS ON THE FORMATION OF COMPOUNDS **2a-c** USING MICROWAVE IRRADIATION AND CONVENTIONAL HEATING

Entry	R	Microwave irradiation (**Method A**)		Conventional heating (**Method B**)		m.p. (ºC)
		Time (min)	Yield (%)*	Time (h)	Yield (%)*	
2a	H	25	70	10	72	231-233
2b	Me	22	73	8	74	195-197
2c	Ph	22	80	8	79	263-265

*Isolated yields.

Method B: The same mixtures as in above were heated on the oil bath at 160 °C for the indicated time. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and boiling ethanol was added. The catalyst was filtrated and the filtrate was concentrated to give the solid product that was recrystallized from ethanol/water to give compounds **2a-c** in 72, 74 and 79 % yields, respectively (Table-1, **method B**).

Reusability of the catalyst: At the end of the reaction, the catalyst could be recovered by a simple filtration. The recycled catalyst washed with ethanol, dried

at 80 ºC for 1 h and reused in another reaction without appreciable reduction in the catalytic activity.

The starting materials **1a-c** were prepared according to the literature method[9]. Firstly, cyclization of 3-(4*H*-1,2,4-triazol-3-ylsulfanyl)-acrylic acids **1a-c** in the presence of H_2SO_4/silica gel using microwave irradiation in solvent-free conditions were explored (**Scheme-I**). Thus, the compounds **1a-c** and H_2SO_4/silica gel were mixed together and then irradiated at 700 W for the indicated time, using a domestic microwave oven Model LG MS-543XD to give the cyclized products 1,2,4-triazolo-[5,1-b][1,3]thiazin-7-ones **2a-c** in good yields (Table-1, **method A**).

For comparison, a classical method for the above mentioned reactions was also investigated by heating the compounds **1a-c** on the oil bath at 160 °C in the presence of H_2SO_4/silica gel (Table-1, **method B**). It was very obvious that the classical approach for these cyclizations have much longer reaction times.

Conclusion

In conclusion, an efficient catalytic method for the cyclization of 3-(4*H*-1,2,4-triazol-3-ylsulfanyl)-acrylic acids into 1,2,4-triazolo[5,1-b][1,3]thiazin-7-ones using sulfuric acid adsorbed on silica gel as catalyst under solvent-free microwave irradiation and conventional heating is reported. The catalyst can be reused after a simple work-up, with a gradual decline of its activity being observed. In comparison, the reactions carried out with the assistance of microwave technique are faster than conventional method.

REFERENCES

1. K. Niknam, *Asian J. Chem*., **17**, 2513 (2005).
2. L. Nagarapu, A.R. Peddiraju and S. Apuri, *Catal. Commun*., **8**, 1973 (2007).
3. M.A. Bigdeli, M.M. Heravi and Gh.H. Mahdavinia, *J. Mol. Catal. A: Chem*., **275**, 25 (2007).
4. S. Kumar and D. Kumar, *Asian J. Chem*., **20**, 4308 (2008).
5. L. Wang and C. Cai, *Monatsh. Chem*., **140**, 541 (2009).
6. A. Davoodnia, *Asian J. Chem*., **22**, 1595 (2010).
7. H.A. Oskooie, M.M. Heravi, A. Sadnia, F. Jannati and F.K. Behbahani, *Monatsh. Chem*., **139**, 27 (2008).
8. A.R. Kiasat, F. Kazemi and K. Nourbakhsh, *Phosphorus Sulfur Silicon Relat. Elem*., **179**, 569 (2004).
9. M.M. Heravi, N. Montazeri, M. Rahimizadeh, M. Bakavoli and M. Ghassemzadeh, *Monatsh. Chem*., **132**, 1225 (2001).
10. N. Montazeri and K. Rad-Moghadam, *Phosphorus Sulfur Silicon Relat. Elem*., **179**, 2533 (2004).
11. N. Montazeri and K. Rad-Moghadam, *Asian J. Chem*., **18**, 1557 (2006).
12. K. Rad-Moghadam and N. Montazeri, *Asian J. Chem*., **19**, 2467 (2007).
13. N. Montazeri and K. Rad-Moghadam, *Chin. Chem. Lett*., **19**, 1143 (2008).
14. K. Rad-Moghadam and N. Montazeri, *Asian J. Chem*., **21**, 499 (2009).
15. F. Hatamjafari and N. Montazeri, *Turk. J. Chem*., **33**, 797 (2009).

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