Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Direct synthesis of thiosulfonic *S*-esters from sulfonic acids using cyanuric chloride under mild conditionsdirect synthesis of thiosulfonic s-esters

B. P. Bandgar[a]; S. S. Pandit[b]
[a] Organic Chemistry Research Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, (M.S), India [b] P.G. Department of Chemistry, Padmashri Vikhe Patil College, Ahmednagar, (M.S), India

To cite this Article Bandgar, B. P. and Pandit, S. S.(2004) 'Direct synthesis of thiosulfonic *S*-esters from sulfonic acids using cyanuric chloride under mild conditionsdirect synthesis of thiosulfonic s-esters', Journal of Sulfur Chemistry, 25: 5, 347 — 350
To link to this Article: DOI: 10.1080/17415990412331317946
URL: http://dx.doi.org/10.1080/17415990412331317946

J. Sulfur Chemistry
Vol. 25, No. 5, October 2004, 347–350

Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

Direct synthesis of thiosulfonic *S*-esters from sulfonic acids using cyanuric chloride under mild conditions

B. P. BANDGAR*,† and S. S. PANDIT‡

†Organic Chemistry Research Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Vishnupuri, Nanded, 431606 (M.S) India
‡P.G. Department of Chemistry, Padmashri Vikhe Patil College, Pravaranagar (Loni. Kd.) Tal. Rahata. Dist. Ahmednagar, 413713 (M.S) India

(*Received 16 April 2004; in final form 24 August 2004*)

A simple, practical method has been developed for the direct synthesis of thiosulfonic S-esters from sulfonic acids and thiols using cyanuric chloride. Good product yields obtained under mild reaction conditions are an important feature of this methodology.

Keywords: Cyanuric chloride; Sulfonic acids; Thiols; Thiosulfonic S-esters; Mild conditions

1. Introduction

Thiosulfonic *S*-esters [1] are powerful sulfenylating agents [2] that react faster, are more stable and easier to handle than sulfenyl chlorides. They are also useful for temporary blocking of mercapto groups in protein chemistry [3] and for industrial applications as biologically active compounds or in polymer production [1]. However, their use has been limited by the lack of easy and practical preparations.

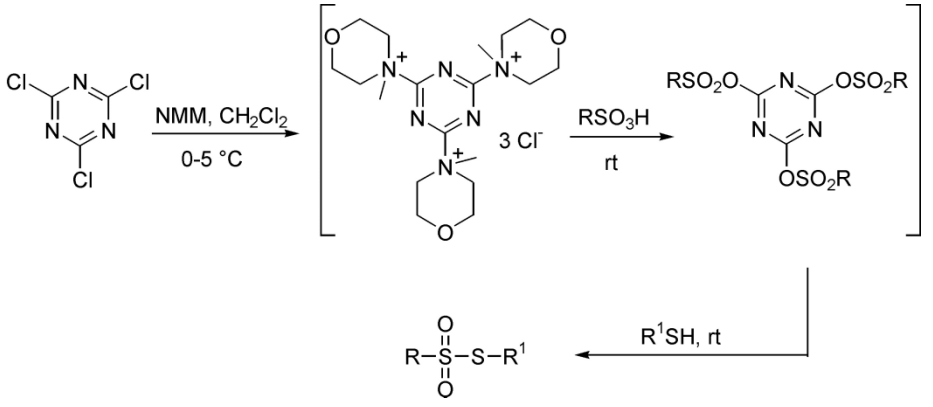
The most often used procedures for the generation of thiosulfonic *S*-esters involve the oxidation of thiols or disulfides [1, 4], and the use of chlorine, bromine or peroxides (*m*-chloroperbenzoic acid, hydrogen peroxide, dinitrogen tetroxide) is often necessary. Few methods are reported from sulfur compounds in a higher oxidation state, involving easily available starting materials [5]. Among these methods are the reduction of sulfonyl halides with potassium iodide [6] or with copper/bronze [7], the reaction with potassium thiosulfonates and diaryliodonium salts [8], the thermolysis of sulfonylhydrazines [9], acetyl chloride-activated zinc reduction of sulfonyl chloride [10], the reaction of sulfinyl chloride with activated Zn refluxing in benzene [11], the treatment of thiosulfinates with $NaIO_4$ [12] and exposure of thiophenols to N_2O_4 [13]. Most of these methods require harsh reaction conditions, long reaction times, and toxic or unstable reagents. The hitherto described method for the direct

* Corresponding author. E-mail: bandgar_bp@yahoo.com

J. Sulfur Chemistry
ISSN 1741-5993 print; ISSN 1741-6000 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/17415990412331317946

conversion of thiosulfonic acids into the corresponding thiosulfonic *S*-esters requires the use of aggressive reagents such as $SOCl_2$. However, some of the reactions are sluggish and yields are generally low.

Hence, these procedures do not appear to be general, efficient and practical. Therefore, it is still necessary to develop a general, efficient and mild method for the direct synthesis of thiosulfonic *S*-esters from the corresponding sulfonic acids. We report here the use of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) for the direct conversion of sulfonic acids into the corresponding thiosulfonic *S*-esters under mild conditions (scheme 1).



SCHEME 1

2. Results and discussion

Various sulfonic acids were activated using cyanuric chloride and *N*-methylmorpholine (NMM). Further, the activated sulfonic acids underwent smooth nucleophilic attack with aryl and aryl alkyl thiols, giving good yields of the corresponding thiosulfonic *S*-esters under mild conditions. The results are summarized in table 1. Even though sterically hindered sulfonic acids required a longer time, they underwent smooth thioesterification under these conditions.

Our method is superior to other methods because the sulfonic acid group can be directly converted into the S-ester moiety at room temperature. This methodology is general, various sulfonic acids such as aliphatic, aromatic and sterically hindered aromatics can be smoothly converted into thiosulfonic S-esters using alkyl, aryl and aryl alkyl thiols under mild reaction conditions.

In conclusion, a convenient and straightforward protocol has been developed to convert sulfonic acids into the corresponding thiosulfonic S-esters under mild conditions. All chemicals used are commercially available and inexpensive.

3. Experimental

3.1 *General procedure*

To a solution of cyanuric chloride (2 mmol) in CH_2Cl_2 (20 ml), *N*-methylmorpholine (7 mmol) was added at 0–5 °C under continuous stirring. This afforded a white suspension, to which a solution of *p*-acetanilide sulfonic acid (6 mmol) was added. After a further 3 h the reaction mixture was filtered through Celite® and to the filtrate *p*-thiocresol (6 mmol) was added at room temperature with constant stirring. After completion of the reaction (TLC), the mixture was washed with 10% sodium bicarbonate (2 × 20 ml). The organic layer was dried with anhydrous sodium sulfate and solvent was removed under reduced pressure to obtain the crude product, which was further purified by column chromatography (light petroleum) (table 1).

Table 1. Synthesis of thiosulfonic *S*-esters from sulfonic acids and thiols using cyanuric chloride.

#	Sulfonic acid	Thiol	Product	Time (min)	Yield (%)[a,b]	Ref.[c]
1	$PhSO_3H$	$Me(CH_2)_5SH$	$PhSO_2S(CH_2)_5Me$	125	79	14
2	$PhSO_3H$	$PhCH_2SH$	$PhSO_2SCH_2Ph$	120	72	14
3	$PhSO_3H$	PhSH	$PhSO_2SPh$	120	74	6
4	$PhSO_3H$	*p*-Me[C_6H_4]SH	$PhSO_2S[C_6H_4]Me$-*p*	100	78	8
5	*p*-Me[C_6H_4]SO_3H	$Me(CH_2)_5SH$	*p*-Me[C_6H_4]$SO_2S(CH_2)_5Me$	130	88	14
6	*p*-Me[C_6H_4]SO_3H	*p*-Cl[C_6H_4]SH	*p*-Me[C_6H_4]$SO_2S[C_6H_4]Cl$-*p*	80	74	8
7	*p*-Me[C_6H_4]SO_3H	PhSH	*p*-Me[C_6H_4]SO_2SPh	45	74	8
8	*p*-Me[C_6H_4]SO_3H	*p*-Me[C_6H_4]SH	*p*-Me[C_6H_4]$SO_2S[C_6H_4]Me$-*p*	75	79	8
9	2,4,6-$(Me)_3[C_6H_2]SO_3H$	PhSH	2,4,6-$(Me)_3[C_6H_2]SO_2SPh$	210	61	14
10	$MeSO_3H$	PhSH	$MeSO_2SPh$	100	70	14
11	*p*-MeC(O)NH[C_6H_4]SO_3H	*p*-Me[C_6H_4]SH	*p*-MeC(O)NH[C_6H_4]$SO_2S[C_6H_4]Me$-*p*	90	77	–[d]

[a]Yield of isolated product. [b]Products characterized by IR, ^{1}H NMR. [c]Published physical and spectral properties. [d]Spectroscopic data of product in entry 11 is given in the Experimental section.

3.2 *Data for p-tolyl p-acetanilidethiosulfonate*

Colorless solid, mp 96–98°C, yield = 77%; IR (KBr) (cm^{-1}): 809, 1078, 1142, 1303, 1328, 1489, 1593, 1680, 3290; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.28 (s, 3H, Ar-CH_3), 2.32 (s, 3H, $COCH_3$), 7.16–7.70 (m, 8H, Ar-H). Elemental analysis (%): calcd. for $C_{15}H_{15}O_2NS_2$ (321.417): C, 56.05; H, 4.70; N, 4.35; S, 19.95. Found: C, 55.92; H, 4.78; N, 4.33; S, 19.64.

Acknowledgment

S. S. P. thanks UGC, New Delhi for a teacher fellowship under the FIP scheme.

References

[1] Zefirov, N. S., Zyk, N. S., Beloglazkina, E. K. and Kutaeladze, A. G. K., 1993, *Sulfur Rep.*, **14**, 223.
[2] (a) Trost, B. M., 1978, *Chem. Rev.*, **78**, 363. (b) Palumbo, G., Ferreri, C., D'Ambrosio, C. and Caputo, R., 1984, *Phosporus Sulfur, Silicon Relat. Elem.*, **19**, 235.
[3] Smith, D. J., Maggio, E. T. and Kenjon, G. L., 1975, *Biochemistry*, **14**, 766.
[4] (a) Arterburn, J. B., Perry, M. C., Nelson, S. L., Dible, B. R. and Holguin, M. S., 1977, *J. Am. Chem. Soc.*, **119**, 9309. (b) Xia, M. and Chen, Z., 1977, *Synth. Commun.*, **27**, 1301.
[5] Lazlo, P. and Mathy, A., 1984, *J. Org. Chem.*, **49**, 2281.
[6] Palumbo, G. and Caputo, R., 1981, *Synthesis*, 888.
[7] Karrer, P., Wehrli, W., Biedermann, E. and Della Vedova, M., 1928, *Helv. Chim. Acta*, **11**, 233.
[8] Xia, M. and Chen, Z., 1997, *Synth. Commun.*, **27**, 1309.
[9] Meier, H. and Menzel, J., 1972, *Synthesis*, 267.
[10] Chemla, F., 1998, *Synlett*, 894.
[11] Freeman, F. and Keindl, M. C., 1983, *Synthesis*, 913.
[12] Takata, T., Kim, Y. H. and Oae, S., 1981, *Bull. Chem. Soc. Jpn.*, 1443.
[13] Oae, S., Kim, Y. H., Fokushima, D. and Takata, T., 1977, *Chem. Lett.*, 893.
[14] (a) Kresze, G. and Kort, W., 1961, *Chem. Ber.*, **97**, 2624. (b) Boldyrev, B. G., Slesarchuk, L. P. and Trofimova, T. A., 1968, *Khim. Seraorg. Soedin Soderzh. Neftyak Nefteprod.*, **8**, 108. (c) Douglass, I. B. and Farah, B. S., 1959, *J. Org. Chem.* **34**, 973. (d) Trost, B. M. and Massiot, G. S., 1977, *J. Am. Chem. Soc.* **99**, 4405.