

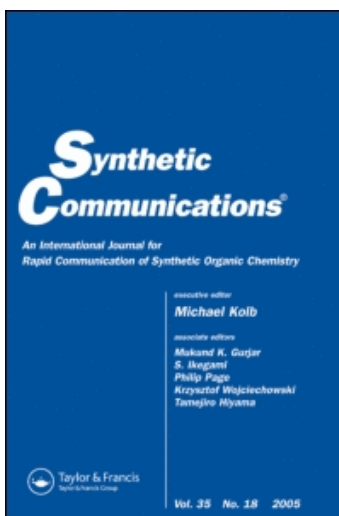
This article was downloaded by:

On: 17 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Synthetic Communications

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597304>

### Sulfur Transfer Reactions of Tetrathiomolybdate in Water: Synthesis of Alkyl Disulfides from Alkyl Halides

Palanichamy Ilankumaran<sup>a</sup>; Kandikere R. Prabhu<sup>a</sup>; Srinivasan Chandrasekaran<sup>a</sup>

<sup>a</sup> Department of Organic Chemistry, Indian Institute of Science, Bangalore, INDIA

**To cite this Article** Ilankumaran, Palanichamy, Prabhu, Kandikere R. and Chandrasekaran, Srinivasan(1997) 'Sulfur Transfer Reactions of Tetrathiomolybdate in Water: Synthesis of Alkyl Disulfides from Alkyl Halides', *Synthetic Communications*, 27: 23, 4031 – 4034

**To link to this Article:** DOI: 10.1080/00397919708005447

**URL:** <http://dx.doi.org/10.1080/00397919708005447>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## SULFUR TRANSFER REACTIONS OF TETRATHIOMOLYBDATE IN WATER: SYNTHESIS OF ALKYL DISULFIDES FROM ALKYL HALIDES

Palanichamy Ilankumaran, Kandikere R. Prabhu and Srinivasan

Chandrasekaran\*

Department of Organic Chemistry, Indian Institute of Science, Bangalore

560 012. INDIA

**Abstract:** Reaction of a number of alkyl halides with tetrathiomolybdate in water as the solvent affords the corresponding disulfides in good yields.

Generally water is not considered as a useful solvent in organic synthesis but surprisingly the use of water as a solvent for conventional organic reactions has found increasing application not only to enhance the rate of reactions but also to perform reactions otherwise impossible.<sup>1</sup> Water is cheap, non toxic and environmentally friendly, and therefore it would be nice if important bond forming reactions can be carried out in water. It is with this perspective that we present our results on a successful sulfur transfer reaction in the synthesis of disulfides from alkyl halides in water.

It has earlier been shown that benzyltriethylammonium tetrathiomolybdate  $[\text{PhCH}_2\text{NEt}_3]_2\text{MoS}_4$ , **1**, in  $\text{CH}_2\text{Cl}_2$  converts alkyl halides in to the cor-

responding disulfides in good yield.<sup>2</sup> Although this methodology works very well in most of the cases, substrates containing carboxyl group pose problems where the decomposition of the reagent is predominant. In order to overcome this problem and to explore the possibility of carrying out this important disulfide bond forming reactions in aqueous medium studies of reactivity of tetrathiomolybdate **1** with alkyl halides in water as the solvent were undertaken.

Accordingly, when sodium salt of  $\omega$ -bromo acid **2** (1mmol) in water was reacted with tetrathiomolybdate **1** (1.1mmol) (25°C, 17h) the reaction proceeded smoothly to give the disulfide **3** in 87% yield after acidification (entry 1, Table I). Similarly when sodium salt of  $\omega$ -bromo hexanoic acid **4** was treated with **1** the corresponding disulfide **5** was isolated in very good yield (84%). A particularly noteworthy example is the reaction of sugar bromide **6** derived from glucose with **1** in water (25°, 72h) giving rise to the sugar disulfide **7** (63%). Although this reaction is slow the formation of the product on the unprotected carbohydrate is quite attractive. Synthesis of similar sugar disulfides has been achieved with great difficulty following a number of steps in low yields.<sup>3</sup> It is also interesting to note that alkyl halides insoluble in water (entry 5-7) also reacted with **1** in aqueous medium to provide the corresponding disulfides in good yields.

It is pertinent to point out that while the same sulfur transfer reaction does not work when ammonium tetrathiomolybdate is used as the reagent, the reaction takes place readily when catalytic amount of benzyltriethylammonium chloride is added to the reaction mixture (entry 2).

In conclusion we have demonstrated that sulfur transfer reactions can indeed be carried out with tetrathiomolybdate **1** in water as the solvent. Easy access to carboxyl group containing disulfides like **3** will be of interest in micellar reactions. The aqueous sulfur transfer reaction with **1** is bound to have application particularly in carbohydrate chemistry.

Table I Reaction of tetrathiomolybdate **1** with alkyl halides in water

Entry	Substrate	Product <sup>a</sup>	Procedure	Time (hrs)	Yield <sup>b</sup> (%)
1			A	17	87
2	"	"	B	20	83
3			A	8	84
4			B	72	63
5			A	5	89
6			A	7	61
7			A	48	60

a. All the products gave satisfactory spectral data.

b. Yield refers to purified products

**Procedure A:** To a stirred solution of bromoacid **2** (1mmol) in water (7ml) Na<sub>2</sub>CO<sub>3</sub> (1.1 mmol) was added. After CO<sub>2</sub> evolution has ceased tetrathiomolybdate **1** (1.1 mmol) was added. After the completion of the reaction, Dil HCl was added and the disulfide **3** was extracted with chloroform and purified by crystallisation (mpt 92°C, lit<sup>4</sup> 93°C).

**Procedure B:** Instead of **1**, ammonium tetrathiomolybdate (1.1 mmol) and benzyltriethylammonium chloride (10 mol%) were used.

**Acknowledgment:** The authors thank the Department of Science and Technology, New Delhi for financial support of this investigation.

**References & notes**

1. A. Lubineau. *Chem & Ind.*, **1996**, 123 and references cited therein.
2. A. R. Ramesha, S. Chandrasekaran. *Synth Commun.*, **1992**, 22, 3277.
3. D. Trimnell, E. Stout, W. M. Doane and C. R. Russell. *J. Org. Chem.*, **1975**, 40, 1337.
4. N. H. Koenig, G. S. Sasin, D. Swern. *J. Org. Chem.*, **1958**, 23, 1525.
5. G. Ivanovics, L. Z. Vargha. *Physiol. Chem.*, **1944**, 281, 156.
6. L. Field, J. E. Lawson, *J. Am. Chem. Soc.*, **1958**, 80, 838.
7. P. Bruin, A. F. Bickel, E. C. Kooyman, *Rec. Trav. Chim.*, **1958**, 71, 1115.

(Received in The Netherlands 17 June 1997)