

This article was downloaded by:

On: 27 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



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

IMPROVED AND CONVENIENT SYNTHESIS OF DISULFIDES IN THE ABSENCE OF SOLVENT CATALYZED BY CLAYFEN

Harshadas M. Meshram^a

^a Indian Institute of Chemical Technology, Hyderabad, India

To cite this Article Meshram, Harshadas M.(1993) 'IMPROVED AND CONVENIENT SYNTHESIS OF DISULFIDES IN THE ABSENCE OF SOLVENT CATALYZED BY CLAYFEN', *Organic Preparations and Procedures International*, 25: 2, 232 – 233

To link to this Article: DOI: 10.1080/00304949309457952

URL: <http://dx.doi.org/10.1080/00304949309457952>

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.

**IMPROVED AND CONVENIENT SYNTHESIS OF DISULFIDES
IN THE ABSENCE OF SOLVENT CATALYZED BY CLAYFEN[†]**

Submitted by Harshadas M. Meshram
(04/07/92)

*Indian Institute of Chemical Technology
Hyderabad 500007, INDIA*

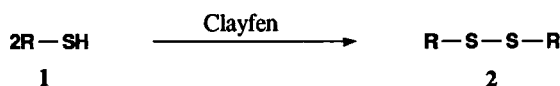
Disulfides are important from both biological and practical points of view.¹ Moreover, the disulfides are used in sulfonylation² of enolates and other anions. The several methods^{3,4} which have been developed for the oxidation of thiols into disulfides, require purification and use of solvent for reaction. More recently, the disulfides have been synthesized using Clayfen and hydrocarbon solvent with heating. However, the large scale manufacture of disulfides is usually fraught with difficulties because of the need for greater quantities of solvent and bigger reactors. Thus, there still is a need for a convenient and economically viable procedure.

Recently, more emphasis has been given to solid-phase reactions⁶ because of their effectiveness and absence of solvent. The growing interest in the clay,⁷ clay supported catalyst⁸ and non-solvent prompted us to synthesize disulfides using Clayfen in the reactions absence of solvent. The yield and purity obtained in the non-solvent reaction is much better than the reported method.⁵ Moreover, the quantity of catalyst used is less compared to an earlier procedure.⁵

TABLE. Oxidation of Thiols to Disulfides

R	Reaction time (hrs)	Yield ^a (%)	mp (bp) ^b (°C)	lit. ^c mp (bp) (°C)
C ₆ H ₅	2	99	60	61-62
4-ClC ₆ H ₄	1.5	99	70-71	71
4-CH ₃ C ₆ H ₄	2	98	46	46
2-NH ₂ C ₆ H ₄	1	92	91-92	93
C ₆ H ₅ CH ₂	2.5	96	72	71-72
CH ₃ (CH ₂) ₁₀ CH ₂	3	91	32	31-34 ^d
HO-CH ₂ CH ₂	3	80	(159-161/01)	(160-162/01) ^e
C ₂ H ₅	2	94	(152-153)	(154)
n-C ₄ H ₉	2	95	(224-226)	(226)

a) All products are characterized by mass, NMR, mp, bp and gave correct HRMS. b) Crystallized from ethanol. c) Ref. 9 unless otherwise noted. d) Ref. 10. e) Ref. 11.



The high yields obtained under mild conditions and its applicability to functionally substituted thiols, coupled the absence side-reactions and the fact that no solvent is required makes the present

procedure economically useful for the large scale synthesis of symmetrical disulfides.

EXPERIMENTAL SECTION

General Procedure.- The thiol (0.01 mol) was mixed with Clayfen¹² (3 g) in mortar-pestle and kept at room temperature for 1-3 hrs with occasional mixing. The paste was then extracted with dichloromethane (3 x 30 mL) and the extract was dried over anhydrous sodium sulfate. Evaporation of the solvent gives pure **2** according to ¹H NMR and tlc analysis.

Acknowledgment.- Author thanks Dr. J. S. Yadav, Head, Organic Division-I, for his interest and encouragement.

REFERENCES

† IICT Communication No. 2919.

1. P. C. Jocelyn, in "Biochemistry of the SH Group", Academic Press, London, New York, 1972.
2. T. Kitamura, J. Nutsyuki and H. Taniguch, *J. Chem. Soc. Perkin Trans.*, **1**, 1607 (1991).
3. T. Sato, J. Otera and H. Nozaki, *Tetrahedron Lett.*, **31**, 3591 (1990); T. J. Wallace, *J. Org. Chem.*, **31**, 3071 (1966); J. Drabowicz and M. Mikolajczyk, *Synthesis*, **32** (1980); A. McKillop and D. Koyunou, *Tetrahedron Lett.*, **31**, 5007 (1990).
4. E. Fristad and R. Peterson, *Synth. Commun.*, **15**, 1 (1985); H. Firouzabadi, N. Iranpoor, H. Pathare, A. Sardarian and J. Toofan, *ibid.*, **14**, 717 (1984).
5. A. Carnelis, N. Depaye, A. Gerstman and P. Laszlo, *Tetrahedron Lett.*, **24**, 3103 (1983); The condition employed an excess of bentonite supported ferric nitrate (0.1 mol thiol and 50 g Clayfen) in 250 mL of solvent with heating.
6. K. Tanaka, S. Kishigami and F. Toda, *J. Org. Chem.*, **56**, 4333 (1991).
7. B. K. G. Theng, "The Chemistry of Clay-Organic Reactions", Adam Hilger, London 1974; H. M. Meshram, *Synth. Commun.*, **20**, 3253 (1990).
8. "Preparative Chemistry Using Supported Reagents", P. Laszlo, Ed., Academic Press, New York, NY, 1987; P. Laszlo, *Acc. Chem. Res.*, **19**, 121 (1986); P. Laszlo, *Science*, **253**, 1473 (1987).
9. R. C. Weast and M. J. Astle, "CRC Handbook Data on Organic Compounds", CRC Press, Inc. Boca Raton, FL, 1988.
10. E. E. Reid, "Organic Chemistry of Bivalent Sulphur Compounds", Vol. 3, p. 395.
11. L. W. Christensen and D. J. Heacock, *Synthesis*, **50** (1978).
12. A. Cornelis and P. Laszlo, *ibid.*, 849 (1980).