

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>

A COMPARATIVE STUDY OF OXIDANTS ON THIOLS

K. Ramadas^a; N. Srinivasan^a; N. Janarthanan^a; R. Pritha^a

^a Centre for Agrochemical Research, SPIC Science Foundation, Madras, INDIA

To cite this Article Ramadas, K. , Srinivasan, N. , Janarthanan, N. and Pritha, R.(1996) 'A COMPARATIVE STUDY OF OXIDANTS ON THIOLS', *Organic Preparations and Procedures International*, 28: 3, 352 – 355

To link to this Article: DOI: 10.1080/00304949609356543

URL: <http://dx.doi.org/10.1080/00304949609356543>

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.

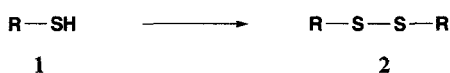
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any 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.

A COMPARATIVE STUDY OF OXIDANTS ON THIOLS†

Submitted by K. Ramadas*, N. Srinivasan, N. Janarthanan and R. Pritha
(01/24/95)

Centre for Agrochemical Research
SPIC Science Foundation
110, Mount Road, Guindy, Madras 600 032, INDIA

A recent article described the synthetic utility of sodium chlorite for the conversion of thiols to disulfides.¹ The present work deals with this transformation using hitherto unreported oxidizing agents. The study compares reaction times, yields and purity of the products using known oxidants with those of the reagents under investigation. The data presented includes a variety of thiols some of which bear other oxidizable functions. Reagents such as sodium metaperiodate, ammonium



R = a) Me₂NC(=S) b) Et₂NC(=S) c) (CH₂)₅NC(=S) d) 2-benzimidazolyl
e) 2-benzothiazolyl f) 2-naphthyl g) phenyl h) 4-tolyl i) 2-aminophenyl
j) 2-carboxyphenyl k) 5-amino-1,3,4-thiadiazolyl l) 4-morpholinyl thiocarbamyl
m) 4-piperidinyl thiocarbamyl n) 4-pyrrolyl thiocarbamyl o) 4-pyrrolidinyl thiocarbamyl
p) 2-benzoxazolyl q) 5-Chlorobenzothiazolyl

persulfate, ceric ammonium nitrate and thionyl chloride so far not studied for this conversion have now been found to furnish high yields of disulfides under simple experimental conditions. The results describe the best conditions which feature short reaction times, quantitative conversion, high purity, process economy and dispensing with the use of solvents. Tetramethylthiuram disulfide and dibenzothiazol-2-yl disulfide are well known fungicides and rubber accelerators used extensively in India and the present work allows the choice of the proper oxidant for large scale production. Ammonium persulfate, chlorite and metaperiodate can be advantageously used in place of chlorine gas, hydrogen peroxide/acid or sodium nitrite/hydrochloric acid for the oxidation to the corresponding disulfides. The use of thionyl chloride on thiols in the presence of pyridine has been reported to furnish dithio-sulfites;² however, our conditions are different as are also the substrates studied for oxidation which makes thionyl chloride the reagent of choice for the oxidation of heterocyclic thiols such as 2-mercapto-benzimidazole, benzoxazole, benzothiazole and similar systems. The results are presented in the Tables. The end products were found to be identical in all respects with authentic samples (Table 3).

EXPERIMENTAL SECTION

Typical Procedure.- To a stirred solution of thiol or dithiocarbamic acid (0.001 m) in THF (5mL) maintained at 10° was introduced an aqueous solution of the oxidant (0.001m, 8mL) in 5 min (thionyl chloride was used as a 5% solution in THF). The product was formed generally in about 20

min. or less (see Tables) as shown by tlc. Dilution with ice water (50 mL) led to the precipitation of the desired disulfide which was collected and dried. It is interesting to note that even aqueous slurries of the substrates were oxidized to the disulfides without any reduction in yield or purity under these conditions.

TABLE 1. Time (min.) and Yields^a (%) of Disulfides from Oxidation of Thiols

Compd	NaClO ₂	H ₂ O ₂ /H ⁺	NaNO ₂ /H ⁺	Cl ₂	(NH ₄) ₂ S ₂ O ₈	NaIO ₄
2a	(20,93)	(20,86)	(25,80)	(25,87)	(15,85)	(5,85)
2b	(20,92)	(25,85)	(30,85)	(25,85)	(20,87)	(5,90)
2c	(20,90)	(25,70)	(20,75)	(15,80)	(15,85)	(5,89)
2d	(15,95)	(20,87)	(25,85)	(20,85)	(15,90)	(5,95)
2e	(15,97)	(20,87)	(20,85)	(20,90)	(15,95)	(5,94)
2f	(15,96)	(20,87)	(25,90)	(20,80)	(10,85)	(5,90)
2g	(10,96)	(15,80)	(15,92)	(10,90)	(10,95)	(5,97)
2h	(10,96)	(15,85)	(10,90)	(10,85)	(10,87)	(5,95)
2i	(15,92)	(15,80)	(15,85)	(15,80)	(10,85)	(5,92)
2j	(10,86)	(15,75)	(15,70)	(15,75)	(10,72)	(5,85)
2k	(15,90)	(20,83)	(20,80)	(20,75)	(15,85)	(20,73)
2l	(15,94)	(25,87)	(25,82)	(20,83)	(15,89)	(10,92)
2m	(15,93)	(20,86)	(25,80)	(20,85)	(15,90)	(15,90)
2n	(20,96)	(25,80)	(20,85)	(25,80)	(20,90)	(15,85)
2o	(15,93)	(20,85)	(20,80)	(20,80)	(15,85)	(15,89)

a) Crude yields with no trace of starting material.

TABLE 2. Time (min) and Yields^a (%) of Disulfides from Oxidation of Thiols

Compd	Ferric Chloride	Ceric ammonium nitrate	Thionyl chloride
2d	(b)	(c, 93)	(15, 94)
2e	(b)	(120, 93)	(10, 93)
2f	(5, 90)	(10, 85)	(10, 80)
2g	(5, 97)	(25, 90)	(5, 96)
2h	(5, 94)	(20, 89)	(10, 90)
2i	(5, 92)	(25, 85)	(b)
2j	(10, 85)	(25, 87)	(b)
2k	(5, 73)	(20, 80)	(b)
2p	(b)	(5, 80)	(20, 82)
2q	(b)	(20, 93)	(25, 91)

a) Crude yields with no trace of starting material. b) No reaction. c) Overnight stirring.

TABLE 3. Mps of Compounds 2a-2q

Cmpd	mp. (°C)	lit mp. (°C)	Cmpd	mp. (°C)	lit mp. (°C)
2a	148	151 ³	2j	285-287	289-290 ⁹
2b	68	70.5 ³	2k	235-237	239 ¹⁰
2c	88-89	86-87 ⁴	2l	148	149-150 ¹¹
2d	200	198 ⁵	2m	78-80	78 ⁹
2e	180-181	182-183 ⁶	2n	93	95-96 ¹²
2f	143	143-144 ⁷	2o	144-146	148 ¹²
2g	65	61-62 ⁸	2p	113-115	112-113 ¹³
2h	47	45-46 ⁸	2q	240	238-242 ¹⁴
2i	78	79-80 ⁶			

Acknowledgement.- The authors thank Professor N. S. Narasimhan, Director, CAR, SSF for providing the facilities. They are indebted to RSIC, IIT, Madras. SPIC Pharma for the spectral data and to the analytical staff of CAR, SSF for mass measurements. N. S. is grateful to the CSIR (SRF), while R. P. thanks the ICAR for a JRF position. We are grateful to Professor K. K. Balasubramanian, I. I. T., Madras for providing some of the substrate samples.

REFERENCES

† This paper is dedicated to **Professor T. R. Govindachari** on the occasion of his 80th birthday.

1. K. Ramadas and N. Srinivasan, *Synth. Commun.*, **25**, 225 (1995) and references therein.
2. L. Field and W. B. Lacefield, *J. Org. Chem.*, **31**, 3555 (1966).
3. R. Rothstein and K. Binpovic *Rec. Trav. Chem. Pays-Bas*, **73**, 561 (1954).
4. W. F. Fischer, R. F. Neu and R. C. Zapp., *Ind. Eng. Chem.*, **51**, 205 (1930).
5. J. G. Everette., *J. Chem. Soc.*, 402, (1930).
6. L. Field and J. E. Lawson., *J. Am. Chem. Soc.*, **80**, 838 (1958).
7. I. B. Douglass and B. S. Farah., *J. Org. Chem.*, **23**, 805 (1953).
8. J. Drabowicz and M. Mikolajczk, *Synthesis*, 32 (1980).
9. *Dictionary of Organic Compounds*, Vol. 2, pp. 2376, 2313, 5th Ed., Chapman Hall, New York.
10. M. Ohta, A. Mufune, T. Higashijima and S. Nagaki, *J. Pharm. Soc. Jpn*, **71**, 1481 (1951).
11. D. Craig, A. E. Juve, W. C. Davidson, W. C. Semon and D. C. Hay, *J. Polymer Sci.*, **8**, 231 (1952).

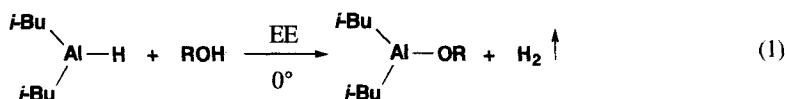
12. B. Oddo and C. Alberti, *Gazz. Chim. Ital.*, **68**, 204 (1938).
13. *Chem. Abstr.*, **54**, 1499a (1960).
14. *Chem. Abstr.*, **57**, 7242g (1962).

SELECTIVE REDUCTION OF α,β -UNSATURATED ALDEHYDES AND KETONES TO ALLYLIC ALCOHOLS WITH DIISOBUTYLALKOXYALANES

Submitted by Jin Soon Cha*, Oh Oun Kwon and Sang Yong Kwon
(12/14/95)

*Department of Chemistry, Yeungnam University
Kyongsan 712-749, Republic of KOREA*

Very recently, we reported that diisobutylchloroalane (DIBAL-Cl) is a highly selective reducing agent for the reduction of enals and enones to the corresponding allylic alcohols,¹ and for the reduction of aldehyde or ketone groups in the presence of many other readily reducible functional groups.² We attributed such a high selectivity to the cyclic mechanism in which the β -hydride of the isobutyl group is shifted to the carbonyl carbon of the substrate:^{1,2} the reduction is very similar to a Meerwein-Ponndorf-Verley type process.³ These unique reactions led us to extend our investigation to the alkoxy derivatives of diisobutylaluminum hydride (DIBAL-H) as a reducing agent. In the course of exploring the reducing action of diisobutylalkoxyalanes (DIBAL-OR), we observed that the reagents are much milder than DIBAL-Cl and effectively reduce aldehydes and ketones under mild conditions. Herein we report the application of these newly synthesized reagents, DIBAL-OR, for the selective reduction of α,β -unsaturated aldehydes and ketones to the corresponding allylic alcohols. The reagents are conveniently prepared by a simple reaction between DIBAL-H and the corresponding alcohols in ethyl ether (EE) solution (Eq 1).



R = Et; DIBAL-OEt, R = *i*-Pr; DIBAL-O^{*i*}Pr, R = *t*-Bu; DIBAL-O^{*t*}Bu

The relative reactivities of DIBAL-OR toward some representative aldehydes and ketones are presented in Table 1. In general, all the alkoxy derivatives examined appear to be much milder than DIBAL-Cl. The relative reactivity of DIBAL-OR is in the order of DIBAL-OEt \geq DIBAL-O^{*i*}Pr > DIBAL-O^{*t*}Bu. Apparently, such a reactivity order arises from the size of the alkoxy substituent. The