

This article was downloaded by:

On: 29 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



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Preparation and Reactivities of the First Isolable Dithiirane, 3-(1,1,3,3-Tetramethyl-4-oxo-4-Phenylbutyl)-3-Phenyldithiirane

Akihiko Ishii^a; Teruo Maruta^a; Tōru Akazawa^a; Juzo Nakayama^a; Masamatsu Hoshino^a

^a Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama, Japan

To cite this Article Ishii, Akihiko , Maruta, Teruo , Akazawa, Tōru , Nakayama, Juzo and Hoshino, Masamatsu(1994) 'Preparation and Reactivities of the First Isolable Dithiirane, 3-(1,1,3,3-Tetramethyl-4-oxo-4-Phenylbutyl)-3-Phenyldithiirane', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 95: 1, 445 — 446

To link to this Article: DOI: 10.1080/10426509408034270

URL: <http://dx.doi.org/10.1080/10426509408034270>

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.

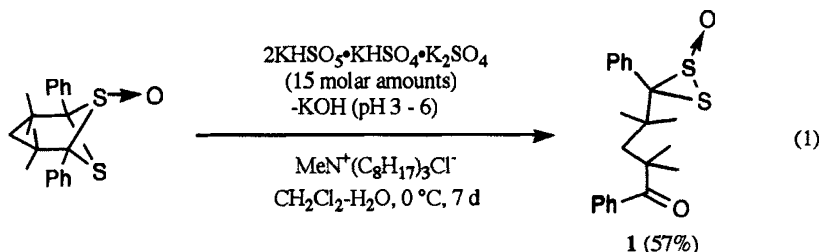
PREPARATION AND REACTIVITIES OF THE FIRST ISOLABLE DITHIIRANE, 3-(1,1,3,3-TETRAMETHYL-4-OXO-4-PHENYLBUTYL)-3- PHENYLDITHIIRANE

AKIHIKO ISHII, TERUO MARUTA, TORU AKAZAWA, JUZO NAKAYAMA,
 AND MASAMATSU HOSHINO
 Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama
 338, Japan

Abstract The reaction of a 4,5-dithiabicyclo[3.1.1]heptane (**3**) with OXONE ($\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) under pH controlled conditions yielded the first isolable dithiirane derivative (**2**) as orange crystals. The structure of the dithiirane was determined by spectroscopic means and X-ray single crystal analysis. Desulfuration, oxidation, and thermal reaction of the dithiirane were examined.

INTRODUCTION

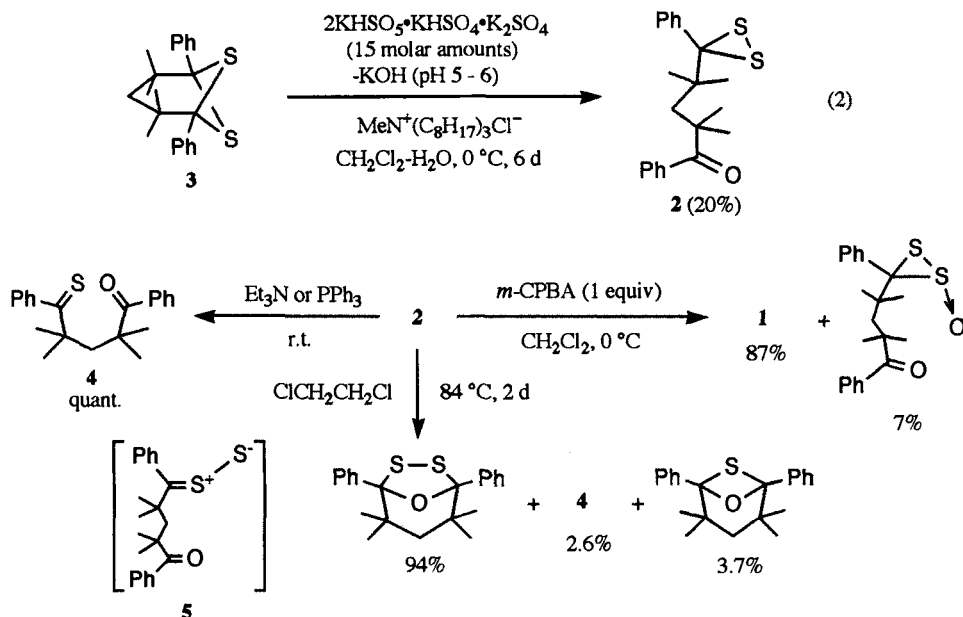
The smallest cyclic disulfides, dithiiranes, are of interest as isomers of thiocarbonyl *S*-sulfides (thiosulfines) and dithioesters.^{1,2} In dithiiranes the 0° dihedral angle leads to significant repulsive lone pair-lone pair interactions in addition to large angle strains,³ and therefore, although several dithiiranes have been recognized as elusive intermediates, no isolable examples including their oxidized derivatives were reported in spite of much effort¹ until our report on **1** had appeared (eq. 1).⁴ We report here synthesis of the first isolable, *unoxidized* dithiirane **2** by oxidation of the bicyclic 1,3-dithietane **3**⁵ with OXONE (Aldrich) ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$)⁶ and its chemical properties including thermal isomerization to the corresponding thiocarbonyl *S*-sulfide.⁷



RESULTS AND DISCUSSION

A CH_2Cl_2 solution of **3**, an aqueous solution of OXONE (pH 5-6), and a catalytic amount of $\text{MeN}^+(\text{C}_8\text{H}_{17})_3\text{Cl}^-$ were mixed up and stirred vigorously at 0°C for 6 days. Careful workup of the mixture allowed the isolation of **2** in 20% yield (eq. 2).

The dithiirane **2** is an orange crystalline compound that is stable at room temperature under air. The structure of **2** was determined by spectroscopic means and X-ray single crystal structure analysis. In the UV-Vis spectrum, the longest absorption maximum was observed at 452 nm (ϵ 104). The observed S-S bond distance was 2.073 Å (X-ray analysis). Dithiirane **2** is rather inert to acidic materials such as *p*-toluenesulfonic acid, but very sensitive to nucleophiles such as amines and phosphines. Reactions of **2** are summarized in Scheme 1. In the thermal reaction, the isomerization of **2** to the corresponding thiocarbonyl *S*-sulfide **5** was suggested.



REFERENCES

1. a) A. Senning, H. C. Hansen, M. F. Abdel-Megeed, W. Mazurkiewicz, and B. Jensen, *Tetrahedron*, **42**, 739 (1986); b) A. Senning, *Sulfur Letters*, **4**, 213 (1986); c) A. Senning, *ibid.*, **11**, 83 (1990); d) G. W. Kutney and K. Turnbull, *Chem. Rev.*, **82**, 333 (1982).
2. R. Huisgen and J. Rapp, *J. Am. Chem. Soc.*, **109**, 902 (1987).
3. (a) J. P. Snyder and L. Carlsen, *J. Am. Chem. Soc.*, **99**, 2931 (1977); (b) S. P. So, *J. Mol. Struct. (Theochem.)*, **148**, 153 (1986); (c) R. M. Wilson, D. N. Buchanan, and J. E. Davis, *Tetrahedron Lett.*, 3919 (1971) and references cited therein.
4. A. Ishii, T. Akazawa, M.-X. Ding, T. Honjo, J. Nakayama, M. Hoshino, and M. Shiro, *J. Am. Chem. Soc.*, **115**, 4914 (1993).
5. A. Ishii, J. Nakayama, M.-X. Ding, N. Kotaka, and M. Hoshino, *J. Org. Chem.*, **55**, 2421 (1990).
6. For oxidation of sulfides with OXONE, see (a) R. J. Kennedy and A. Stock, *J. Org. Chem.*, **25**, 1901 (1960); (b) B. M. Trost and D. P. Curran, *Tetrahedron Lett.*, **22**, 1287 (1981).
7. A. Ishii, T. Akazawa, T. Maruta, J. Nakayama, M. Hoshino, and M. Shiro, *Angew. Chem. Int. Ed. Engl.*, **33**, 777 (1994).