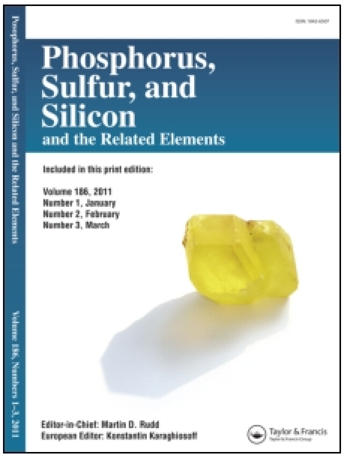

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Preparation and Reactivities of the First Isolable Dithiirane, 3-(1,1,3,3-Tetramethyl-4-oxo-4-Phenylbutyl)-3-Phenyldithiirane

Akihiko Ishii[a]; Teruo Maruta[a]; Töru Akazawa[a]; Juzo Nakayama[a]; Masamatsu Hoshino[a]
[a] Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama, Japan

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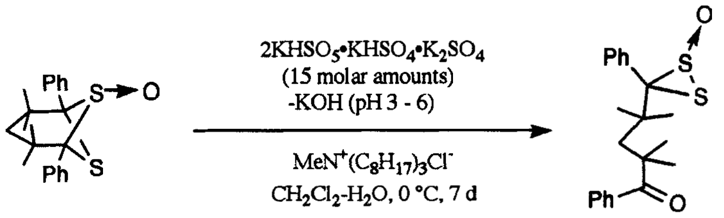
PREPARATION AND REACTIVITIES OF THE FIRST ISOLABLE DITHIIRANE, 3-(1,1,3,3-TETRAMETHYL-4-OXO-4-PHENYLBUTYL)-3-PHENYLDITHIIRANE

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 ($KHSO_5$•$KHSO_4$•K_2SO_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-rey 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 effort[1] 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) ($2KHSO_5$•$KHSO_4$•K_2SO_4)[6] and its chemical properties including thermal isomerization to the corresponding thiocarbonyl *S*-sulfide.[7]



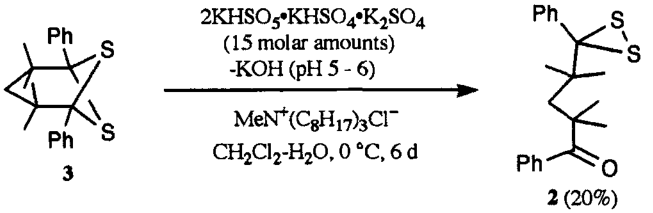
(1)

1 (57%)

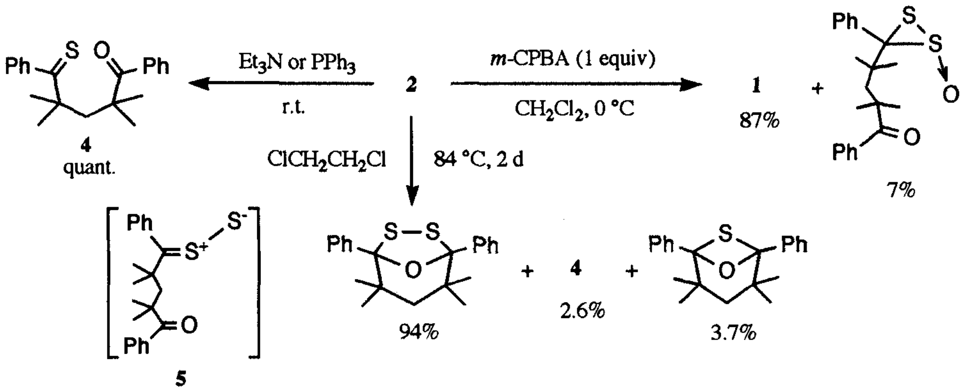
RESULTS AND DISCUSSION

A CH_2Cl_2 solution of **3**, an aqueous solution of OXONE (pH 5~6), and a catalytic amount of $MeN^+(C_8H_{17})_3Cl^-$ 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 absoption 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.



(2)



SCHEME 1

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