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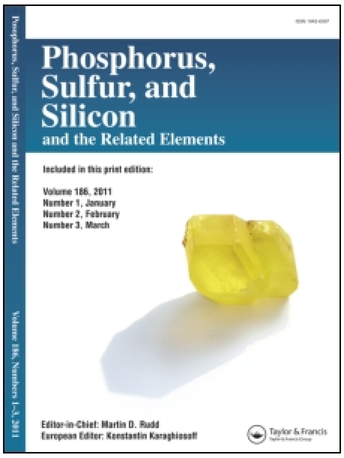

Phosphorus, Sulfur, and Silicon and the Related Elements

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Syntheses, Structures, and Thermolyses of Tetracoordinate $1,2\Lambda^4$-Oxathietanes

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To cite this Article Kawashima, Takayuki , Ohno, Fumihiko and Okazaki, Renji(1994) 'Syntheses, Structures, and Thermolyses of Tetracoordinate $1,2\Lambda^4$-Oxathietanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 439 — 440

To link to this Article: DOI: 10.1080/10426509408034268

URL: http://dx.doi.org/10.1080/10426509408034268

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Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 439–440
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SYNTHESES, STRUCTURES, AND THERMOLYSES OF TETRACOORDINATE 1,2λ^4-OXATHIETANES

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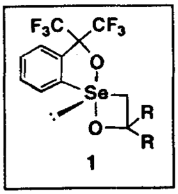
Abstract Title compounds were synthesized by oxidative cyclization of the corresponding dihydroxy sulfide with bromine in the presence of triethylamine. The X-ray crystallographic analysis of 3-phenyl derivative shows that it has a distorted trigonal bipyramidal structure. Thermolysis gave no olefin, but instead benzhydryl phenyl ketone, benzophenone, and the corresponding cyclic sulfenate and thioketal were formed. A trace of 2,2,3-triphenyloxirane was also formed. The mechanism is discussed.

INTRODUCTION

In the course of our investigations on oxetanes bearing a highly coordinate main group element at the neighboring position, we have recently reported syntheses and crystal structures of tetracoordinate 1,2-oxaselenetanes **1**.[1] Interestingly, thermolyses of oxaselenetanes **1** yielded neither olefins nor oxiranes, in sharp contrast to the oxetanes containing group 14 and 15 elements.[2] In this paper we wish to describe the title compounds **2**, sulfur analogues of **1**, as a novel type of sulfuranes.

RESULTS AND DISCUSSION

Sequential treatment of sulfide **3** with *n*-BuLi in the presence of DABCO and then with carbonyl compound **5** or **6** gave β-hydroxyalkyl sulfide **7a** or **7b**. A similar treatment of *t*-butyldimethylsilyl (TBS) ether **4** with LDA and then **5**, followed by desilylation with *n*-Bu_4NF, yielded **7c**. Compounds **7a-c** were treated with 1 equiv Br_2 in the presence of 2 equiv Et_3N (CCl_4, r.t.) to afford 1,2λ^4-oxathietanes **2a-c** with recovery of some **7a-c**.



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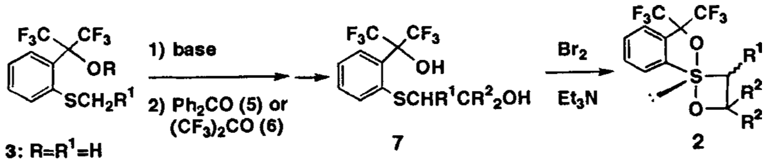


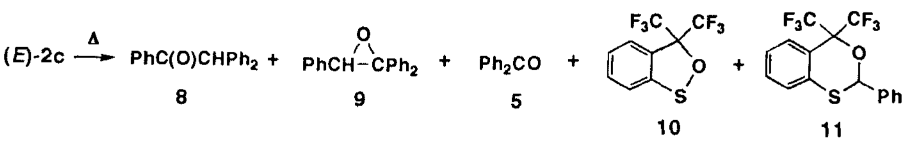
3: R=R^1=H
4: R=TBS, R^1=Ph

7

2

a: R^1=H, R^2=Ph; b: R^1=H, R^2=CF$_3$; c: R^1=R^2=Ph

Oxathietanes **2a** and **2b** were very moisture-sensitive and readily hydrolyzed in air, whereas a diastereomeric mixture (4:1) of **2c** could be purified by flash column chromatography on silica gel to give single diastereomer (*E*)-**2c**. The X-ray crystallographic analysis of (*E*)-**2c** indicates that it has a structure very similar to that of oxaselenetane **1** and that the phenyl group at the 3-position is *cis* against the lone pair of sulfur atom (Fig. 1). This is the first example for a tetracoordinate 1,2λ^4-oxathietane. Two oxygen atoms occupy apical positions, while two carbon atoms and a lone pair occupy equatorial positions. The four-membered ring is almost planar, which is a common structural feature of such oxetanes.[1,2]



Thermolysis ($CDCl_3$, 155 °C, 17 h) of (*E*)-**2c** afforded phenyl-migrated ketone **8** (47%), benzophenone (**5**) (33%), cyclic sulfenate **10** (52%) and cyclic thioketal **11** (31%). The formation of a trace of oxirane **9** was confirmed by ^{1}H NMR spectroscopy. As in the case of the oxaselenetane, thermolysis of oxathietane (*E*)-**2c** did not give an olefin, indicating that the bond energy of a chalcogen-oxygen double bond is not sufficient to undergo a Wittig-type reaction even for a sulfur-oxygen bond. Taking into consideration the previous and present results,[1] it can be reasonably con-cluded that heterolysis of the S-O bond of the four-membered ring becomes a key step of this thermolysis. Further investigations on the formation mechanism of an oxirane are in progress.

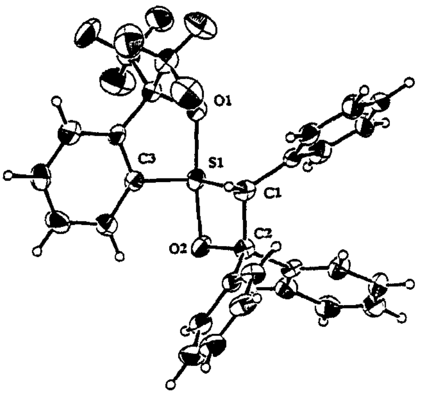


Fig. 1. ORTEP drawing of (*E*)-**2c**.

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