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Synthesis, Crystal Structure, and Thermolysis of a Pentacoordinate $1,2\lambda^6$-Oxathietane: An Intermediate of the Corey−Chaykovsky Reaction of Oxosulfonium Ylides?

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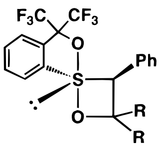
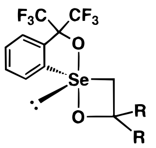
Oxetanes bearing highly coordinate main group elements at the position adjacent to the oxygen atom have been well-known as intermediates or transition states of very important reactions in organic synthesis such as the Wittig and Peterson reactions.[1] In our research on such oxetanes, we have synthesized pentacoordinate 1,2-oxaphosphetanes,[2a,b] 1,2-oxasiletanide,[2c] 1,2-oxagermetanide,[2d] and 1,2-oxastannetanide,[2e] *i.e.*, intermediates of the Wittig and Peterson-type reactions. We recently found that tetracoordinate $1,2\lambda^4$-oxathietane **1a**[3a] $1,2\lambda^4$-oxaselenetane **2**,[3b] which have structures similar to those of the above group 14 and 15 element analogues, yielded no olefins on heating. Specifically, in the case of **1a**, bearing a tetracoordinate sulfur, a small amount of an oxirane was observed in the reaction mixture. This unique result prompted us to examine the reactivity of such oxetanes bearing a *pentacoordinate* sulfur which can be regarded as an intermediate of the Corey−Chaykovsky reaction[4] of oxosulfonium ylides with carbonyl compounds. We now report on the synthesis, crystal structure, and thermolysis of the first example of stable pentacoordinate $1,2\lambda^6$-oxathietane **3b**, a novel type of sulfurane oxide.[5]



1a: R = Ph
1b: R = CF$_3$



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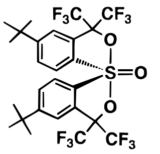

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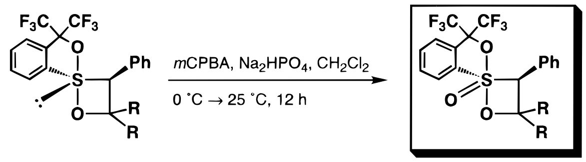
Oxidation of tetracoordinate $1,2\lambda^4$-oxathietanes **1a** and **1b**[3a] with *m*CPBA in the presence of Na_2HPO_4 (CH_2Cl_2, 0 °C → 25 °C, 12 h) gave the corresponding pentacoordinate $1,2\lambda^6$-oxathietanes **3a** and **3b**, respectively (Scheme 1).[6] Although the 3,4,4-triphenyl derivative **3a** was observed spectroscopically, its isolation was unsuccessful because of its instability, while the 3-phenyl-4,4-bis(trifluoromethyl) derivative **3b** could be purified by flash column chromatography (18%) with a recovery of **1b** (17%).[7] Recrystallization of **3b** from ether gave colorless plates which melted at 139.5−141.1 °C with decomposition.

Scheme 1



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3

a: R = Ph, b: R = CF$_3$

In the ^{1}H NMR spectrum of **3b**, the proton ortho to sulfur of the Martin ligand[5a,8] resonated at a low field (δ 8.70), which is one of the features of compounds with a trigonal bipyramidal (TBP) structure.[2a,c,d,3,9] A downfield shift from **1b** (δ 6.39) to **3b** (δ 6.87) was observed for the methine proton on the four-membered ring. In the ^{13}C NMR spectra downfield shifts from **1b** (δ_{CH} 87.66, $\delta_{ipso\text{-}\mathrm{C}}$ 136.63) to **3b** (δ_{CH} 100.76, $\delta_{ipso\text{-}\mathrm{C}}$ 140.23) were observed for the methine carbon and the *ipso*-carbon adjacent to the central sulfur. These downfield shifts seem attributable to the increased electropositivity of the central sulfur of **3b** compared with **1b**.

The X-ray crystallographic analysis of **1b** (Figure 1) and **3b** (Figure 2)[10] indicated that they have distorted TBP structures which are very similar to each other. The two oxygen atoms of the oxathietane ring and the Martin ligand occupy the apical positions, while two carbon atoms and a lone pair (for **1b**) or an exocyclic oxygen atom (for **3b**) occupy the equatorial positions. The phenyl group at the 3-position is *cis* to the lone pair of sulfur (for **1b**) or to the ecxocyclic oxygen (for **3b**), indicating that the oxidation of sulfurane **1b** proceeds with retention of configuration. The apical S−O bonds are bent away from the lone pair (**1b**) or the equatorial oxygen (**3b**), leading to the deviation of the O−S−O angles by 10.75(9)° and 18.6(3)° from linearity for **1b** and **3b**, respectively. The large deviation in the range 10−20° is a common structural feature of the hypervalent species containing a four-membered ring.[2,3] The equatorial S−O bond length of **3b** (1.445(6) Å) is similar to that of sulfurane oxide **4** (1.439(4) Å), considerably shorter than that of sulfoxides.[5b] The oxathietane ring of **1b** is slightly

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[1] For the Wittig reactions, see: (a) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 2, pp 1316−1329. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863−927. For the Peterson reactions, see: (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 58−73. (d) Ager, D. J. *Org. React. (N.Y.)* **1990**, *38*, 1−223. For the Peterson-type reactions, see: (e) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410−429. (f) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; pp 176−177.

[2] (a) Kawashima, T.; Kato, K.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 4008−4110. Kawashima, T.; Kato, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 869−870. (b) Kawashima, T.; Takami, H.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 4509−4510. (c) Kawashima, T.; Iwama, N.; Okazaki, R. *Ibid.* **1992**, *114*, 7598−7599. (d) Kawashima, T.; Nishiwaki, Y.; Okazaki, R. *J. Organomet. Chem.* **1995**, *499*, 143−146. (e) Kawashima, T.; Iwama, N.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2507−2508.

[3] (a) Kawashima, T.; Ohno, F.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2094−2095. (b) Kawashima, T.; Ohno, F.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115,* 10434−10435.

[4] For the Corey−Chaykovsky reactions, see: (a) Aubé, J. In *Comprehensive Organic Synthesis: Selectivity, Strategy, and Efficiency in Modern Synthetic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 1, pp 822−825. For the related reactions of aminosulfoxonium ylides, see: (b) Johnson, C. R. *Acc. Chem. Res.* **1973**, *6*, 341−347.

[5] For previous examples of sulfurane oxides, see: (a) Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 3155−3168. (b) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *Ibid.* **1974**, *96*, 6735−6744. (c) Lau, P. H. W.; Martin, J. C. *Ibid.* **1977**, *99*, 5490−5491. (d) Rongione, J. C.; Martin, J. C. *Ibid.* **1990**, *112*, 1637−1638.

[6] Use of some other oxidizing reagents such as RuO_4, ozone, and dimethyldioxirane was unsuccessful.

[7] A complex reaction mixture including some unidentified products was obtained. **3b**: colorless plates, mp 139.5−141.1 °C dec; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.87 (s, 1H), 7.43−7.55 (m, 3H), 7.73 (d, $J = 7.5$ Hz, 2H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.89 (t, $J = 7.8$ Hz, 1H), 7.93 (t, $J = 7.8$ Hz, 1H), 8.70 (d, $J = 7.8$ Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ 74.91 (sept, $^2J_{\mathrm{CF}} = 32$ Hz), 80.74 (sept, $^2J_{\mathrm{CF}} = 32$ Hz), 100.76 (s), 120.98 (q, $^1J_{\mathrm{CF}} = 287$ Hz), 121.16 (q, $^1J_{\mathrm{CF}} = 287$ Hz), 121.61 (q, $^1J_{\mathrm{CF}} = 287$ Hz), 122.26 (q, $^1J_{\mathrm{CF}} = 288$ Hz), 125.97 (s), 127.26 (s), 128.89 (s), 129.29 (s), 130.19 (m), 130.59 (s), 131.12 (s), 133.14 (s), 136.58 (s), 140.23 (s). Anal. Calcd for $C_{19}H_{10}F_{12}O_3S$: C, 41.77; H, 1.84; S, 5.87. Found: C, 41.70; H, 2.08; S, 6.35.

[8] This bidentate ligand is very effective in stabilizing the higher coordination states of nonmetallic elements; see: Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049−1053.

[9] Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2711−2715.

[10] **1b**: $C_{19}H_{10}F_{12}O_2S$, FW = 530.33, crystal dimensions (mm) 0.50 × 0.50 × 0.30, orthorhombic, space group *Pbca*, $a = 18.096(2)$ Å, $b = 19.682(2)$ Å, $c = 11.329(3)$ Å, $V = 4034(1)$ Å^3, $Z = 8$, $D_{\mathrm{calcd}} = 1.746$ g/cm^3, $R = 0.044$, ($R_{\mathrm{w}} = 0.026$). **3b**: $C_{19}H_{10}F_{12}O_3S$, FW = 546.33, crystal dimensions (mm) 0.50 × 0.20 × 0.30, monoclinic, space group $P2_1/c$, $a = 10.522(7)$ Å, $b = 17.045(5)$ Å, $c = 12.491(5)$ Å, $\beta = 106.91(3)°$, $V = 2143(1)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.693$ g/cm^3, $R = 0.075$, ($R_{\mathrm{w}} = 0.049$). Full details of the crystallographic structure analyses are described in the supporting information.

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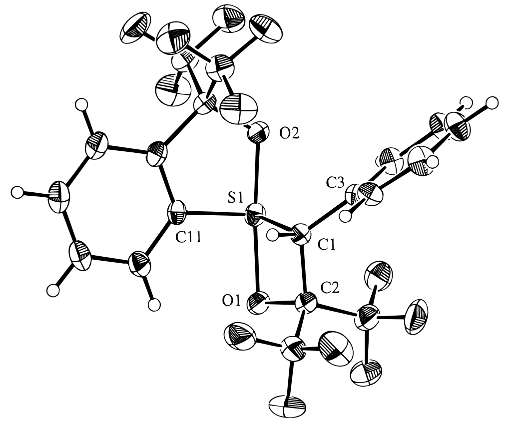


Figure 1. ORTEP drawing of **1b** with thermal ellipsoid plot (30% probability for all non-hydrogen atoms). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): S1−O1, 1.901(2); S1−O2, 1.781(2); S1−C1, 1.859(3); S1−C11, 1.789(3); C1−C2, 1.548(4); C2−O1, 1.394(3); O1−S1−O2, 169.25(9); C1−S1−O1, 73.1(1); S1−C1−C2, 90.1(2); C1−C2−O1, 99.0(2); S1−O1−C2, 93.3(2); O2−S1−C11, 88.3(1); C1−S1−C11, 105.1(1); S1−C1−C2−O1, 17.9(2); O1−S1−C1−C2, −13.5(2).

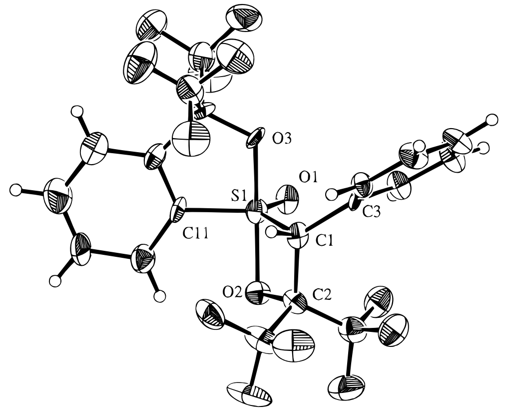


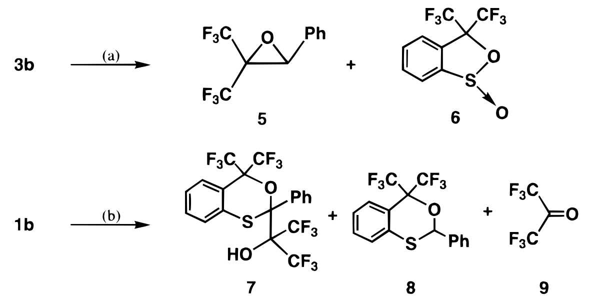
Figure 2. ORTEP drawing of **3b** with thermal ellipsoid plot (30% probability for all non-hydrogen atoms). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): S1−O1, 1.445(6); S1−O2, 1.822(7); S1−O3, 1.744(7); S1−C1, 1.852(8); S1−C11, 1.77(1); C1−C2, 1.57(1); C2−O2, 1.40(1); O2−S1−O3, 161.4(3); C1−S1−O2, 74.8(4); S1−C1−C2, 90.2(6); C1−C2−O2, 97.4(8); S1−O2−C2, 96.9(6); O3−S1−C11, 88.2(5); C1−S1−C11, 121.4(4); O1−S1−C1, 121.2(4); O1−S1−C11, 117.0(4); O1−S1−O2, 97.6(4); O1−S1−O3, 98.8(4); S1−C1−C2−O2, 6.8(7); O2−S1−C1−C2, −5.4(6).

puckered (S−C−C−O 17.9(2)°), while that of **3b** is almost planar (S−C−C−O 6.8(7)°).

Thermolysis ($CDCl_3$, 100 °C, 100 min in a degassed sealed tube) of **3b** gave oxirane **5** (85%) and cyclic sulfinate **6** (97%). The mild conditions and simplicity in the thermolysis products are in marked contrast to those of tetracoordinate 1,2λ^4-oxachalcogenetanes.[3] The thermolysis ($CDCl_3$, 155 °C, 29 h) of **1b** afforded a somewhat complicated mixture of cyclic thioacetal **7** (84%), **8** (11%), and hexafluoroacetone (**9**) (8%) (Scheme 2).

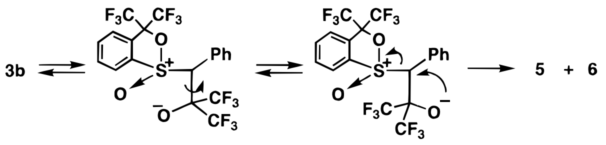
These results have revealed an interesting difference in reactivity between oxetanes with a tetracoordinate sulfur and those with a pentacoordinate sulfur. In both cases, the first step of the reaction can be considered to be the S−O bond cleavage of the four-membered rings. Since cyclic sulfinate **6** is a better leaving group than the corresponding cyclic sulfenate, it can be reasonably explained that oxirane formation readily occurs in the case of **3b** (Scheme 3), while a 1,3-proton shift[11] followed by a Pummerer rearrangement is favored in the case of **1b**.

Scheme 2^a



^{a} (a) $CDCl_3$, 100 °C, 100 min. (b) $CDCl_3$, 155 °C, 29 h.

Scheme 3



Although the oxetanes containing a pentacoordinate group 14 or 15 element gave an olefin,[2] the oxathietane **3b** having a pentacoordinate sulfur yielded an oxirane. This indicates that the thermal reactivity mainly depends on the bond energy of the oxygen and the central atom. The oxathietane **3b** can be regarded as an equivalent to a *syn*-betaine which is formed by the *syn* addition of the polarized $C^-{-}S^+$ bond of an oxosulfonium ylide to the C═O bond of a carbonyl compound. The relative facility of the *syn* addition compared with the *anti* addition can be expected in terms of electrophilic assistance at the oxygen center in the course of the Corey−Chaykovsky reaction.[12] Therefore, oxirane formation from **3b** strongly suggests a possibility that pentacoordinate 1,2λ^6-oxathietanes are intermediates in the addition step of the Corey−Chaykovsky reaction.

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Supporting Information Available: Physical and spectral data for **1b**, **3a**,**b**, **5**, **6**, and **7**, an experimental procedure for the synthesis of **3b**, and X-ray crystallographic data with tables of thermal and positional parameters, bond lengths, and bond angles for **1b** and **3b** (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) A similar 1,3-proton shift was observed in the thermolysis of **2**.[3b]

(12) A theoretical study has reported that there is no activation energy for the *syn* addition, while there is a 10.6 kcal/mol barrier for the *anti* addition in the case of sulfonium ylide $H_2S{=}CH_2$ with formaldehyde; see: Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1987**, *109*, 1−14.