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The First 2,2-Dialkoxythiirane

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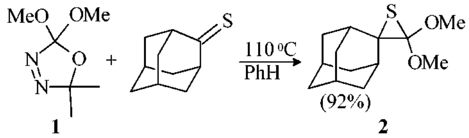
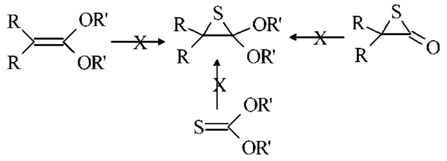
ABSTRACT



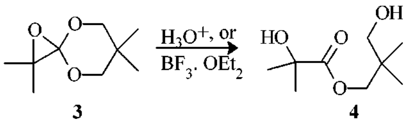
Thermolysis of 1 at 110 °C in benzene containing adamantanethione leads to thiirane 2 in 92% yield, as an isolable, stable solid. Compound 2 is the first example of the hitherto unknown 2,2-dialkoxythiiranes. It shows some reactions characteristic of thiiranes.

Reactions of electrophilic carbenes with thiocarbonyl compounds are believed to occur through intermediate thiocarbonyl ylides which, in the absence of a trapping agent, typically undergo 1,3-electrocyclization to a thiirane.[1] In the case of thiocarbonyl ylides with a suitably placed carbonyl group, a 1,5-dipolar cyclization to form a 1,3-oxathiole is preferred.[2] Recently, a convenient preparation of chlorinated thiiranes from nonenolizable thioketones and chlorocarbenes was described.[3] In general, however, the preparation of thiiranes by reaction of carbenes with C═S double bonds is uncommon. Although potential precursors of 1,1-dialkoxythiiranes, such as ketene acetals, thionocarbonates, and some thiiranones[4] (Scheme 1), are known, 1,1-dialkoxythiiranes have never been reported. They can be expected to be acid-sensitive compounds, by analogy to the properties of the corresponding dialkoxyoxiranes (ortho esters).[5] One oxirane of a ketene acetal (2,2,6,6-tetramethyl-1,4,8-trioxabicyclo-[2.5]octane, **3**) had been isolated, after numerous attempts. It was stable toward bases, but it opened readily to give **4** under the influence of aqueous acid or BF_3 etherate[5c] (Scheme 2). The ortho ester **5** also hydrolyzed readily, to yield the corresponding α-hydroxy ester **6**[5a] as might be expected of such strained compounds (Scheme 3).

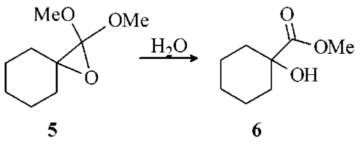
Scheme 1



Scheme 2



Scheme 3



We now report the isolation (92% yield) of the first 2,2-dialkoxythiirane (**2**)[6] from the reaction of dimethoxycarbene,

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[1] For a recent review, see: Mlostoñ, G.; Heimgartner, H. *Polish J. Chem.* **2000**, *74*, 1503.

[2] Kelmendi, B.; Mlostoñ, G.; Heimgartner, H. *Heterocycles* **2000**, *52*, 475.

[3] Mlostoñ, G.; Romanski, J.; Swiatek, A.; Heimgartner, H. *Helv. Chim. Acta* **1999**, *82*, 946.

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formed by thermolysis of oxadiazoline **1**,[7] with adamantanethione. The single-crystal X-ray structure of thiirane **2** shows that the C2−S bond is of normal length (1.8499(17) Å) as compared to the C−S bonds in 4e-chloro-2,2′-epithio-2-(2′-adamantyl)adamantane (**7**, 1.850(9) and 1.847(9) Å, Figure 1).[8] Similarly, the S1−C3 bond length (1.8671(16) Å) and the C2−C3 bond length in **2** (1.470(2) Å vs 1.50(1) Å in **7**) are normal. These results suggest that the C2−S bond of **2** is not highly polar, as might be imagined of a compound that could have an elongated bond to reduce strain, as in **8**, because the partial charges could be stabilized, Figure 1. Ring opening reactions of **2** presumably involve H-bonding to water (for example) or coordination of another electrophile to S of the thiirane.

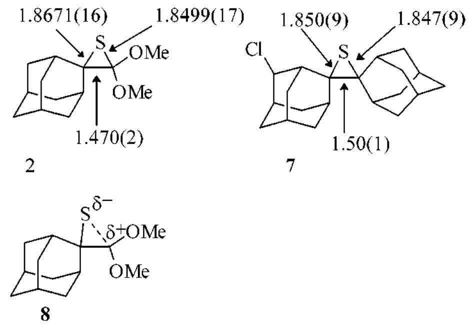
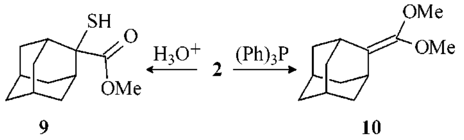


Figure 1. Selected bond lengths (Å) in **2** and in the model **7**.

Thiirane **2** could be handled without special care to exclude moisture, but it did hydrolyze quantitatively to the α-mercapto ester **9**[9] upon treatment with aqueous trifluoroacetic acid. Desulfurization of **2**, upon treatment with triphenylphosphine, was also quantitative to afford the dimethyl acetal of ketene **10** (Scheme 4). The known diethyl analogue[10] of **10** served as a model for the identification of **10**.

Scheme 4



Acknowledgment. The authors thank Dr. J. F. Britten (McMaster University) for the X-ray work. M.D and J.W. also thank the NSERC for financial support, and G.M. acknowledges support by the Polish State Committee for Scientific Research (Grant 3 T09A 007 16).

Supporting Information Available: Details of the crystal and molecular structures of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Mlostoñ, G.; Gendek, T.; Heimgartner, H. *Helv. Chim. Acta* **1998**, *81*, 1585 and references therein.

(5) 2,2-Dialkoxyoxiranes, which we thought to be unknown before the year 2001, are quite rare. (a) Dawid, M.; Venneri, P. C.; Warkentin, J. *Can. J. Chem.* **2001**, *79*, 110. (b) Rakhmankulov, D. L.; Zlotskii, S. S.; Imashev, U. B.; Uzikova, V. N.; Zlotskii, S. N.; Karakhanov, R. A. U.S.S.R. Pat. 707918, 1980; *Chem. Abstr*. **1980**, *93*, 46690. (c) Newman, M. S.; Kilbourn, E. *J. Org. Chem.* **1970**, *35*, 3186.

(6) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.79−2.02 (broad m, 14H), 3.61 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 26.8, 27.6, 35.9, 36.1, 37.0, 37.2, 57.7, 66.6, 115.0.

(7) (a) El-Saidi, M.; Kassam, K.; Pole, D. L.; Tadey, T.; Warkentin, J. *J. Am. Chem. Soc.* **1992**, *114*, 8751. (b) Wong, T.; Warkentin, J.; Terlouw, J. K. *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 33. (c) Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 2454. (d) Win, W. W.; Kao, M.; Eiermann, M.; McNamara, J. J.; Wudl, F.; Pole, D. L.; Kassam, K.; Warkentin, J. *J. Org. Chem.* **1994**, *59*, 5871. (e) Pole, D. L.; Warkentin, J. *J. Org. Chem.* **1997**, *62*, 4065. (f) Rigby, J. H.; Laurent, S.; Cavezza, A.; Heeg, M. J. *J. Org. Chem.* **1998**, *63*, 5587. (g) Rigby, J. H.; Cavezza, A.; Heeg, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 3664. (h) Muchall, H. M.; Werstiuk, N. H.; Choudhury, B.; Ma, J.; Warkentin, J.; Pezacki, J. P. *Can. J. Chem.* **1998**, *76*, 238. (i) Dunn, J. A.; Pezacki, J. P.; McGlinchey, M. J.; Warkentin, J. *J. Org. Chem.* **1999**, *64*, 4344. (j) Butler, D. N.; Halton, B.; Warkentin, J.; Warrener, R. N. *Aust. J. Chem.* **2000**, *53*, 561. (k) Venneri, P. C.; Warkentin, J. *Can. J. Chem.* **2000**, *78*, 1194.

(8) Tolstikov, G. A.; Lerman, B. M.; Umanskaya, L. I. *Tetrahedron Lett.* **1980**, *21*, 4189.

(9) Identified by means of ^{1}H and ^{13}C NMR spectroscopy as well as mass spectrometry.

(10) Van Schaik, T. A. M.; Henzen, A. V.; van der Gen, A. *Tetrahedron Lett.* **1983**, *24*, 1303.