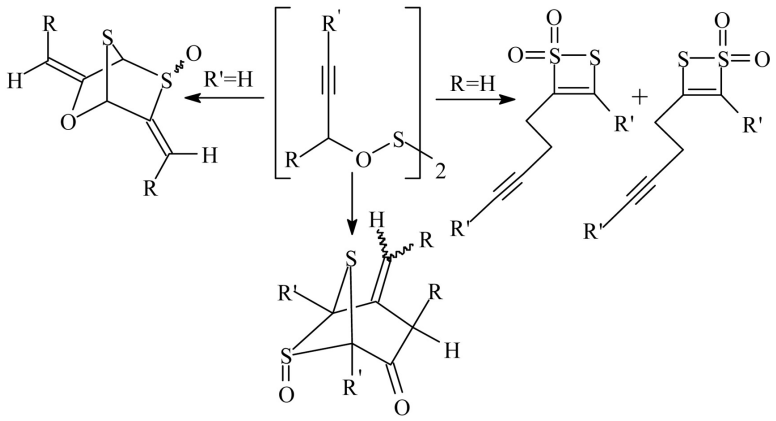
Communication

New Structures from Multiple Rearrangements of Propargylic Dialkoxy Disulfides

Samuel Braverman, Tatiana Pechenick, Hugo E. Gottlieb, and Milon Sprecher

J. Am. Chem. Soc., **2003**, 125 (47), 14290-14291• DOI: 10.1021/ja036962y • Publication Date (Web): 04 November 2003



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
COMMUNICATIONS

Published on Web 11/04/2003

New Structures from Multiple Rearrangements of Propargylic Dialkoxy Disulfides

Samuel Braverman,* Tatiana Pechenick, Hugo E. Gottlieb, and Milon Sprecher

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

Received June 29, 2003; E-mail: bravers@mail.biu.ac.il

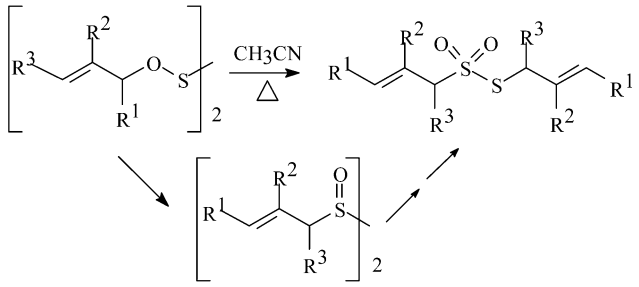
The field of sigmatropic rearrangements of allylic and propargylic esters of sulfur acids at various oxidation states has proven to be a rich source of synthetically valuable and mechanistically intriguing reactions, often yielding novel and surprising products.[1] Herein we report on some additional examples of this type, namely, the formation and characterization of the heretofore unknown structures of types **10**, **11**, **14**, and **15**.

The reported failure of Thompson[2] notwithstanding, we have recently succeeded in developing the necessary methodology to prepare allylic[3] and propargylic[4] dialkoxy disulfides in high yield and have found them to be stable in $CHCl_3$ solution at −18 °C for extended periods. In refluxing acetonitrile, diallyloxy disulfides undergo double [2,3]-sigmatropic rearrangement to *vic*-disulfoxides, which spontaneously rearrange to the appropriate bis(allyl) thiosulfonates, as expected (Scheme 1).[3,5,6]

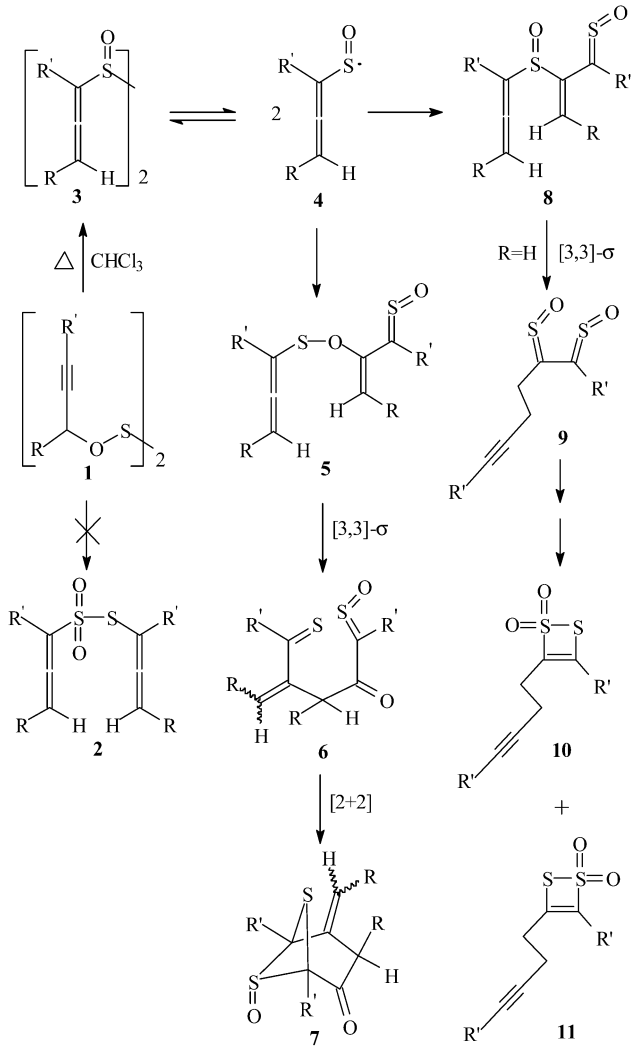
By parallel series of reactions, dipropargyloxy disulfides would have been expected to yield bis(allenyl) thiosulfonates (**2**). In fact, however, the first isolated products were found to have a new and unusual type of structure.[4] They were 6,7-dithiabicyclo[3.1.1]-heptane-2-one-6-oxides (**7**; Scheme 2) incorporating the 1,3-dithiacyclobutane-1-oxide moiety recently identified by Block[7] in the zwiebelanes isolated from freshly cut onion.

Apparently, the presence of the additional double bonds in the allenyl groups diverts the reaction from the path of Scheme 1 at the disulfoxide stage. A careful examination and exacting workup of the chloroform solution of **1a** (**1**, R═R′ = H; Scheme 2) following 7 h reflux showed that **7a** was accompanied by two isomeric products. These were individually isolated and on the basis of extensive spectroscopic determinations, which included full analysis of ^1H and ^{13}C NMR data with the aid of 2D techniques such as COSY, NOESY, HMQC, and HMBC, as well as IR and HRMS, were assigned the surprising structures **10a** and **11a** (**10**, **11**, R═R′ = H; Scheme 2).[8] The two regioisomers can be distinguished by comparing the chemical shifts of the olefinic carbons (C-1 and C-2; these are identified by their long-range C−H interactions), since the main effect of the thiosulfonate function is deshielding of the carbon β to the sulfonyl group and shielding of the carbon β to the sulfide atom. The ratio of **7a**/**10a**/**11a** isolated was 32:3:14, respectively (combined yield, 49%). Substitution at C-γ of the propargyl moieties significantly improved the isolated yields and affected the ratio of products. Thus, the rearrangement of **1b** (**1**, R = H, R′= CH_3CH_2−) led to **7b**, **10b**, and **11b**, individually isolated, in yields of 10, 41, and 34%, respectively. Sterically demanding substituents at these positions slowed the reaction but had an even more marked effect on yield and product composition. After 25 h reflux in chloroform, **1c** (**1**, R = H, R′ = $(CH_3)_3C$−; Scheme 2) yielded only 8% of **7c** and 92% of **10c**, and **1d** (**1**, R = H, R′ = $(CH_3)_3Si$−; Scheme 2) after 20 h yielded 57% **10d** and 19% **11d**, but no **7d**. The α,β-unsaturated four-membered cyclic thiosulfonate grouping present in **10** and **11** appears to have been unknown to date, though compounds having a saturated four-membered ring thiosulfonate function have been reported previously[7a,9] as the products of dimerization of sulfines which is

Scheme 1

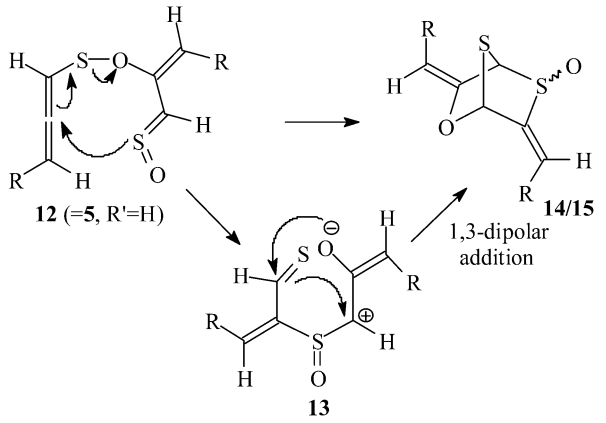


Scheme 2



10.1021/ja036962y CCC: $25.00

Scheme 3



followed by intramolecular disproportionation. A number of a priori reasonable mechanisms may be proposed for the formation of **7**, **10**, and **11**. However, applying Occam's razor, we tentatively suggest the reaction path of Scheme 2. As in Scheme 1, a double [2,3]-sigmatropic rearrangement converts **1** to an α-disulfoxide, **3**, which dissociates to two allenyl sulfinyl radicals, **4**.[5a] Sulfinyl radicals are known to be capable of reacting either at the oxygen or the sulfur atom.[5] Recombination of two such radicals via the sulfinyl oxygen of one and C-2 of the other gives **5**, which converts to **7** by tandem [3,3]-sigmatropic rearrangement (**5** → **6**) and [2 + 2] cycloaddition (**6** → **7**). Alternatively, two radicals **4** recombine via the sulfinyl sulfur of one and C-2 of the other to yield **8** (Scheme 2). It appears that the stable conformation of **4**, permitting conjugative stabilization of the free radical and distancing the sulfinyl oxygen from the allenyl π-electrons, is one in which approach to oxygen is hindered when R′ is bulky. This may be the rationale for the preferential reaction of the sulfur in such cases. The [3,3]-sigmatropic rearrangement of **8** produces the disulfine **9**, intramolecular disproportionation of which in a manner analogous to that found in the intermolecular dimerization of sulfines[7a,9] and in the conversion of α-disulfoxides to thiosulfonates[5,6] leads to **10** and **11**.

We have previously reported that α-substituted dipropargyloxy disulfides such as **1e** (**1**, R = CH_3−, R′ = H; Scheme 2) rearranged relatively rapidly (2 h, refluxing chloroform) to a mixture of the *Z* and *E* isomers of **7e**. No evidence for accompanying **10e** or **11e** was found. Investigating the possible effect of bulky α-substituents, we were astounded at the vagary of this system. The rearrangements of **1f** (**1**, R = $(CH_3)_3C$−, R′ = H; Scheme 2) and **1g** (**1**, R = adamantyl−, R′ = H; Scheme 2) were rapid, as was **1e**, but the two isomeric products obtained and chromatographically separated in each case, were *not* derivatives of structures **7**, **10**, or **11**. Extensive spectroscopic determinations as detailed above for the latter led to the identification of the two pairs of isomers as **14f**/**15f** (**14**/**15**, R = $(CH_3)_3C$−; Scheme 3; yield 57%) and **14g**/**15g** (**14**/**15**, R = adamantyl−; Scheme 3; yield 62%), the components of each pair differing from each other in the stereochemistry of the sulfoxide group, exo or endo.[10] Heating overnight in chloroform solution led to interconversion of the isomers of each pair, presumably by pyramidal inversion of the sulfoxide function. Each isomer separately led to the same equilibrium mixture (e.g., the equilibrium ratio of **14f** to **15f** was 2:5).

The stereochemistry of the two double bonds in structure **14**/**15** was established by NOESY experiments, which showed a strong interaction of the respective bridgehead hydrogens with the nearby *tert*-butyl or adamantyl hydrogens but no interaction with the vinyl hydrogens.

In these last cases, the reaction path of Scheme 2 is abandoned at the point of the [3,3]-sigmatropic rearrangement of **5**, possibly because it would involve incipient allylic steric interactions of the bulky substituents. Instead, it seems, the allenic carbon of **12** bonds to the sulfinyl sulfur with concomitant cleavage of the other S−O bond (**12** → **13**). Though this proposed bond rearrangement may be rationalized in various ways, we suggest that it be viewed as a homologous hetero-Cope rearrangement in which the delocalized cross-conjugated 2-oxyallyl-1,3-dipole produced in **13** replaces a simple C═C π-bond. Structure **14**/**15** is accessible from **13** by an internal 1,3-dipolar addition to the thione double bond.

The 3,6-dialkylidene-2-oxa-5,7-dithiabicyclo[2.2.1]heptane 5-oxide structure **14**/**15** appears to have no precedence in the literature, though Baudin[11] has reported the isolation of a 3,6-dialkylidene-2-oxa-5,7-dithiabicyclo[2.2.1]heptane 5,5-dioxide from the acid treatment of a *N*-morpholino 3,3-disubstituted propa-1,2-dienesulfinamide.

A more detailed discussion of mechanistic and steric considerations, as well as the results of ongoing investigations, will be presented in the full article.

Acknowledgment. This research was supported by the Israel Science Foundation (Grant No. 280/01-1).

Supporting Information Available: Experimental procedures and full spectroscopic data for all new compounds (**10a/11a**, **10b/11b**, **10c**, **10d/11d**, **14f/15f**, and **14g/15g**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Braverman, S. In *Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: New York, 1988; Chapter 13. (b) Braverman, S. In *Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: New York, 1988; Chapter 14. (c) Braverman, S. In *The Chemistry of Sulfinic Acids, Esters and Their Derivatives*; Patai, S. Ed.; Wiley: New York, 1990; Chapter 11. (d) Braverman, S. in *The Chemistry of Sulfenic Acids and Their Derivatives*, Patai, S. Ed.; Wiley: New York, 1990; Chapter 8.
(2) Thompson, Q. E.; Crutchfield, M. M.; Dietrich, M. W.; Pierron, E. *J. Org. Chem.* **1965**, *30*, 2692−2696.
(3) Braverman, S.; Pechenick, T. *Tetrahedron Lett.* **2002**, *43*, 499−502.
(4) Braverman, S.; Pechenick, T.; Gottlieb, E. H. *Tetrahedron Lett.* **2003**, *44*, 777−780.
(5) (a) Freeman, F. *Chem. Rev.* **1984**, *84*, 117−135. (b) Lacombe, S. M. *Rev. Heteroat. Chem.* **1999**, *21*, 1−41.
(6) A recent paper, Gregory, D. D.; Jenks, W. S. *J. Phys. Chem. A* **2003**, *107*, 3414−3423, disputes the previous proposal that the conversion of the intermediate sulfenyl sulfinate to the thiosulfonate proceeds by a free radical mechanism.
(7) (a) Block, E. *Angew. Chem., Int. Ed. Engl*. **1992**, *31*, 1135−1178. (b) Block, E.; Thiruvazhi, M.; Toscano, P. J.; Bayer, T.; Grisoni, S.; Zhao, S. H. *J. Am. Chem. Soc*. **1996**, *118*, 2790−2798. (c) Block, E.; Bayer, T.; Naganathan, S.; Zhao, S. H. *J. Am. Chem. Soc.* **1996**, *118*, 2799−2810.
(8) For spectral data for **10a**/**11a**, **10b/11b**, **10c**, and **10d/11d**, see Supporting Information.
(9) (a) Block, E.; Bazzi, A. A.; Revelle, L. K. *J. Am. Chem. Soc.* **1980**, *102*, 2490−2491. (b) Baudin, J.-B.; Commenil, M.-G.; Julia, S. A.; Wang, Y. *Bull. Soc. Chim. Fr.* **1996**, *133*, 515−529. (c) For a general review on sulfines, see: Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 1−27.
(10) For spectral data for **14f**/**15f** and **14g**/**15g**, see Supporting Information.
(11) Baudin, J.-B.; Julia, S. A.; Ruel, O.; Toupet, L.; Wang, Y. *Bull. Soc. Chim. Fr.* **1995**, *132*, 79−85.

JA036962Y