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### New Structures from Multiple Rearrangements of Propargylic Dialkoxy Disulfides

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## New Structures from Multiple Rearrangements of Propargylic Dialkoxy Disulfides

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*Sundry dipropargyloxy disulfides have been successfully prepared and their rearrangement paths and products have been found to be dependent upon their substitution pattern. Inter alia compounds of two heretofore unknown structure types—10 and 11 on the one hand and 14 and 15 on the other—have been obtained and characterized.*

**Keywords** Cycloaddition; propargylic dialkoxy disulfides; sigmatropic rearrangement; sulfine; synthesis; thioaldehyde

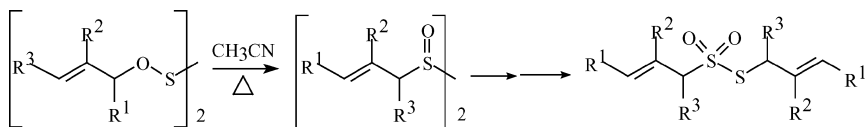
The field of sigmatropic rearrangements of allylic and propargylic esters of sulfur acids at various oxidation states has proven to be a rich source of synthetically valuable and mechanistically intriguing reactions, often yielding novel and surprising products.<sup>1</sup> Herein we report on some additional examples of this type, namely, the formation and characterization of the heretofore unknown structures of types **10**, **11**, **14**, **15**, and **16**.

The reported failure of Thompson<sup>2</sup> notwithstanding, we have recently succeeded in developing the necessary methodology to prepare allylic<sup>3</sup> and propargylic<sup>4</sup> dialkoxy disulfides in high yield and have found them to be stable in CHCl<sub>3</sub> 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).<sup>3,5,6</sup>

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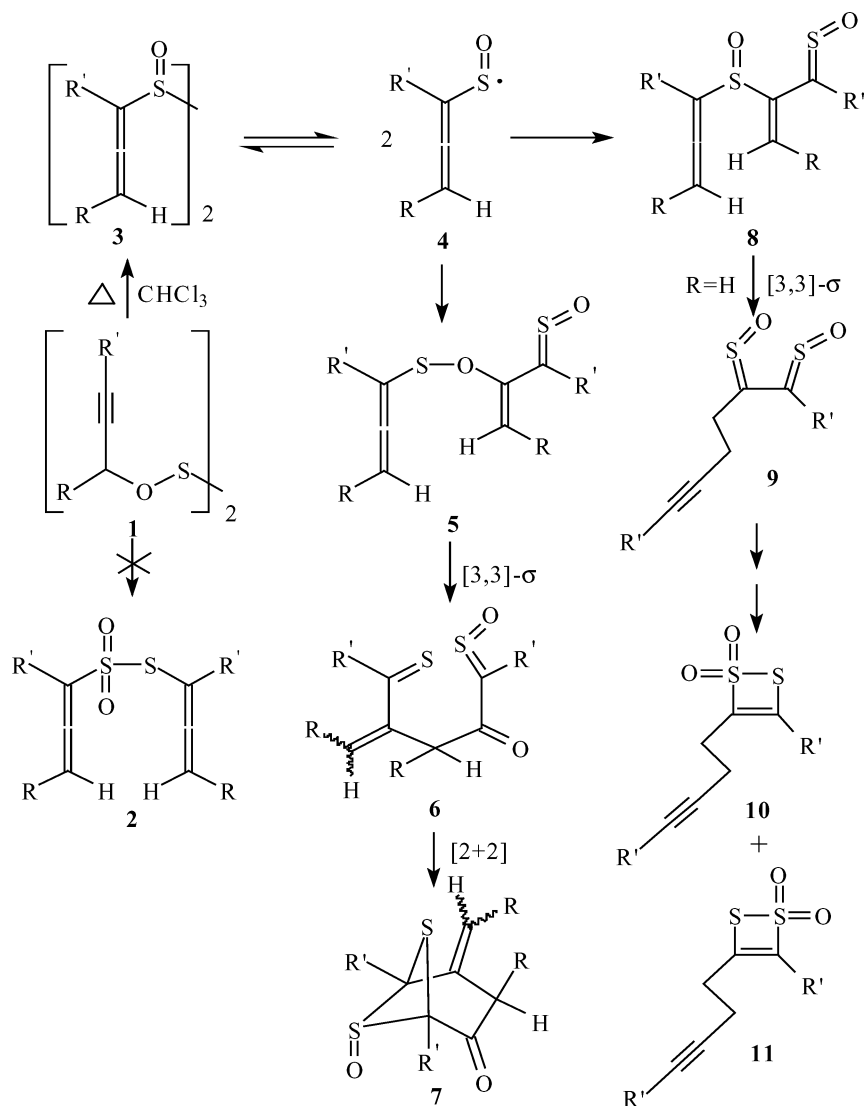
Address correspondence to Samuel Braverman, Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel. E-mail: braverman@mail.biu.ac.il



SCHEME 1

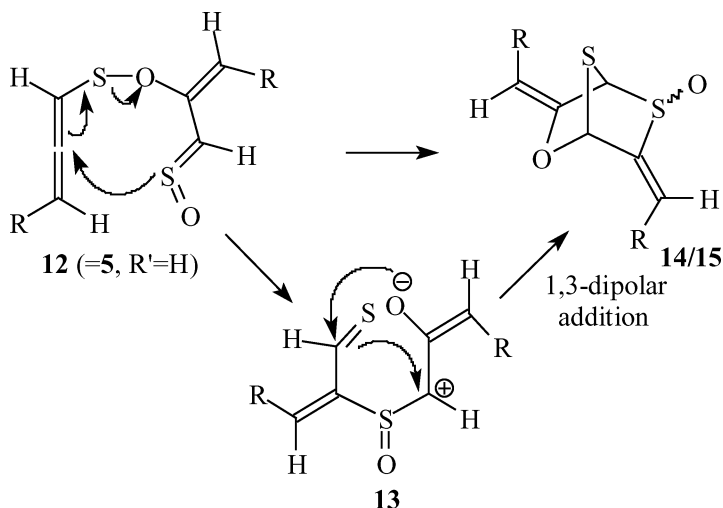
By parallel series of reactions, dipropargyloxy disulfides would have been expected to yield bis(allenyl) thiosulfonates (**2**). In fact, however, the first isolated products were found to have a new and unusual type of structure.<sup>4a</sup> They were 6,7-dithiabicyclo[3.1.1]-heptane-2-one-6-oxides (**7**; Scheme 2) incorporating the 1,3-dithiacyclobutane-1-oxide moiety recently identified by Block<sup>7</sup> 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 disulfide 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 surprising isomeric products, **10a** and **11a** (**10**, **11**, R = R' = H; Scheme 2).<sup>4b</sup> 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<sub>3</sub>)<sub>3</sub>C-; Scheme 2) yielded only 8% of **7c** and 92% of **10c**, and **1d** (**1**, R = H, R' = (CH<sub>3</sub>)<sub>3</sub>Si-; Scheme 2) after 20 h yielded 57% **10d** and 19% **11d**, but no **7d**. 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  $\alpha$ -disulfoxide, **3**, which dissociates to two allenyl sulfinyl radicals, **4**.<sup>5a</sup> Sulfinyl radicals are known to be capable of reacting either at the oxygen or the sulfur atom.<sup>5</sup> 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**  $\rightarrow$  **6**) and [2 + 2] cycloaddition (**6**  $\rightarrow$  **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  $\pi$ -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<sup>7a,8</sup> and in the conversion of  $\alpha$ -disulfoxides to thiosulfonates<sup>5,6</sup> leads to **10** and **11**.



SCHEME 2

We have previously reported that  $\alpha$ -substituted dipropargyloxy disulfides such as **1e** (**1**,  $R = \text{CH}_3$ -,  $R' = \text{H}$ ; 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  $\alpha$ -substituents, we were astounded



SCHEME 3

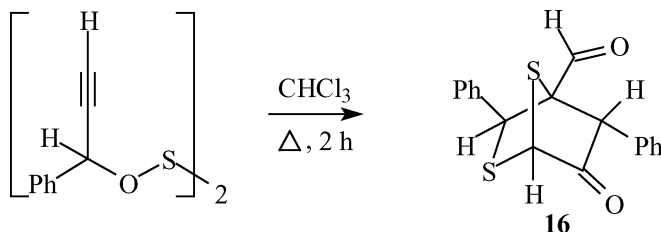
at the vagary of this system. The rearrangements of **1f** (**1**, R = (CH<sub>3</sub>)<sub>3</sub>C-, R' = H; Scheme 2) and **1g** (**1**, R = adamantyl-, R' = H; Scheme 2) were rapid, as was **1e**, but the two isomeric products obtained and chromatographically separated in each case were *not* derivatives of structures **7**, **10**, or **11**. Extensive spectroscopic determinations led to the identification of the two pairs of isomers as **14f/15f** (**14/15**, R = (CH<sub>3</sub>)<sub>3</sub>C-; 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*. 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 Nuclear Overhauser Effect Spectroscopy (NOESY) experiments, which showed a strong interaction of the respective bridge-head 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**).

Structure **14/15** is accessible from **13** by an internal 1,3-dipolar addition to the thione double bond.

In continuation, we have now found that in the case of the  $\alpha$ -phenylpropargyl ester a new member of this family of products, 6-oxo-3,5-diphenyl-2,7-dithiabicyclo[2.2.1] heptane-4-carbaldehyde (**16**, Scheme 4), is formed. A possible mechanism for the last reaction will also be presented.



SCHEME 4

## REFERENCES

- [1] a) S. Braverman, in *Chemistry of Sulfones and Sulfoxides*, S. Patai, Z. Rappoport, and C. J. M. Stirling, Eds. (Wiley: New York, 1988), Chap. 13; b) S. Braverman, in *Chemistry of Sulfones and Sulfoxides*, S. Patai, Z. Rappoport, and C. J. M. Stirling, Eds. (Wiley: New York, 1988), Chap. 14; c) S. Braverman, in *The Chemistry of Sulfinic Acids, Esters and Their Derivatives*, S. Patai, Ed. (Wiley: New York, 1990), Chap. 11; d) S. Braverman, in *The Chemistry of Sulfinic Acids and Their Derivatives*, S. Patai, Ed. (Wiley: New York, 1990), Chap. 8.
- [2] Q. E. Thompson, M. M. Crutchfield, M. W. Dietrich, and E. Pierron, *J. Org. Chem.*, **30**, 2692–2696 (1965).
- [3] S. Braverman and T. Pechenick, *Tetrahedron Lett.*, **43**, 499–502 (2002).
- [4] a) S. Braverman, T. Pechenick, and H. E. Gottlieb, *Tetrahedron Lett.*, **44**, 777–780 (2003); b) S. Braverman, T. Pechenick, H. E. Gottlieb, and M. Sprecher, *J. Am. Chem. Soc.*, **125**, 14291–14292 (2003).
- [5] a) F. Freeman, *Chem. Rev.*, **84**, 117–135 (1984); b) S. M. Lacombe, *Rev. Heteroat. Chem.*, **21**, 1–41 (1999).
- [6] A recent paper, D. D. Gregory and W. S. Jenks, *J. Phys. Chem. A*, **107**, 3414–3423 (2003), disputes the previous proposal that the conversion of the intermediate sulfenyl sulfinate to the thiosulfonate proceeds by a free radical mechanism.
- [7] a) E. Block, *Angew. Chem., Int. Ed. Engl.*, **31**, 1135–1178 (1992); b) E. Block, M. Thiruvazhi, P. J. Toscano, T. Bayer, S. Grisoni, and S. H. Zhao, *J. Am. Chem. Soc.*, **118**, 2790–2798 (1996); c) E. Block, T. Bayer, S. Naganathan, and S. H. Zhao, *J. Am. Chem. Soc.*, **118**, 2799–2810 (1996).
- [8] a) E. Block, A. A. Bazzi, and L. K. Revelle, *J. Am. Chem. Soc.*, **102**, 2490–2491 (1980); b) J.-B. Baudin, M.-G. Commenil, S. A. Julia, and Y. Wang, *Bull. Soc. Chim. Fr.*, **133**, 515–529 (1996); c) For a general review on sulfines, see B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **101**, 1–27 (1982).