# Reactivity Pattern of Bis(propargyloxy) Disulfides: Tandem Rearrangements and Cyclizations

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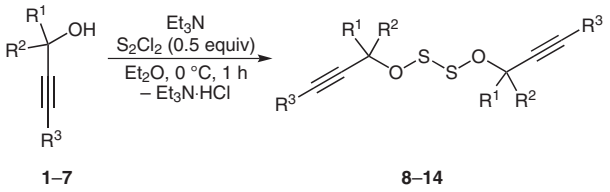
**Abstract:** Thirty-five substituted bis(propargyloxy) disulfides were successfully prepared in good to excellent yields, and their reactivity was found to be strongly dependent on the substitution pattern of the reactant. Inter alia they undergo surprising tandem sigmatropic rearrangements and cycloadditions. Three heretofore unknown product types were isolated and fully characterized: 6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxide derivatives, two isomeric 1,2-dithiete 1,1-dioxides (α,β-unsaturated four-membered cyclic thiosulfonates) from bis(propargyloxy) disulfides with α- or γ-alkyl-substituted propargyl groups, and two isomeric 2-oxa-5,7-dithiabicyclo[2.2.1]heptane 5-oxides from bis(propargyloxy) disulfides with α-*tert*-butyl- or α,α-dialkyl-substituted propargyl groups.

**Key words:** sigmatropic rearrangements, cycloadditions, substituent effects, bis(propargyloxy) disulfides, dithiabicyclic structures, organosulfur chemistry, thiosulfonates, *vic*-disulfoxides

Although dialkoxy disulfides have been known since 1895,[1] they have received little attention until recently.[2–5] They were first prepared by the reaction of sulfur monochloride ($S_2Cl_2$) with a suspension of the sodium alkoxide in ligroin,[1] but this procedure was not suitable for higher molecular weight homologues. More recently, the reaction of sulfur monochloride with alcohols in dichloromethane solution in the presence of triethylamine was reported to yield primary and secondary saturated dialkoxy disulfides.[6] However, no pure dialkoxy disulfides of tertiary saturated alcohols were obtained. It was further reported that the product from propargyl alcohol decomposed below room temperature and that during attempted distillation diallyloxy disulfide disproportionated to acrolein, allyl alcohol, and elemental sulfur.[6]

We recently reported in preliminary communications the successful preparation of both diallyloxy[7a,b] and bis(propargyloxy) disulfides[7a,c,d] in good to excellent yields. This success was putatively attributed to the modified preparative procedure (diethyl ether as solvent, reaction temperature of 0 °C, and low-temperature workup), in the course of which the chloride ion produced is precipitated as triethylamine hydrochloride (Scheme 1). Cleavage of the S–S bond in the product is thus avoided.

Herein we report the extension of this synthetic approach to the preparation of further variously substituted bis(propargyloxy) disulfides (Table 1). Most of the new compounds of relatively low molecular weight have a strong pungent smell of crushed onion in the case of diallyloxy disulfides, and of garlic in the case of bis(propargyloxy) disulfides. All compounds were identified by their spectral data. Primary bis(propargyloxy) disulfides exhibit the characteristic NMR splitting pattern of diastereotopic α-methylene protons, while secondary bis(propargyloxy) disulfides are obtained as a mixture of four diastereomers due to restricted rotation around the S–S bond.[3a,6]




**Scheme 1**

It was found that the bis(propargyloxy) disulfides (Table 1) are unstable at room temperature, but stable in chloroform solution at –18 °C for extended periods. The unsubstituted bis(propargyloxy) disulfide (**8**) is more stable than the α-substituted bis(propargyloxy) disulfides (e.g., **9a–h**, **12a–g**) and less stable than the γ-substituted ones (e.g., **10a–h**). A series of unstable bis(propargyloxy) disulfides **9a–h**, **12a–g** (Table 1) derived from aliphatic secondary propargylic alcohols were successfully isolated. Of the secondary bis(propargyloxy) disulfides bearing aromatic α-substituents, only the bis(α-phenylpropargyloxy) disulfide (**13**) was actually isolated, at –15 °C, in 41% yield; its reactivity could not be established yet, probably due to its instability. In contrast to the influence of α-substituents on the stability of the bis(propargyloxy) disulfides, substituents at the γ-carbon, especially bulky ones (cf. **10g**, see Tables 1 and 3) or an aromatic one (cf. **11j**, see Table 1) greatly increase stability. The preparation of **14** derived from a tertiary propargyl alcohol **7** required special conditions because of its propensity to undergo immediate rearrangement (see Scheme 8 below).

While diallyloxy disulfides were found to rearrange in refluxing acetonitrile solution to thiosulfonates **16** (Scheme 2),[7a,b] presumably via a double [2,3]-sigmatropic rearrangement to the unstable[8] *vic*-disulfoxides, the rearrangement of the bis(propargyloxy) disulfides did not lead to the corresponding thiosulfonates. In fact, it was found and reported in preliminary communications[7c,d] that different examples of the class of reactants under discussion

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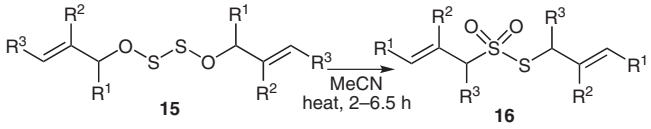
led to products of differing structural types. No less than three such types were encountered. Apparently, the reaction path strongly depends on the substitution pattern of the reactants. To provide a firm basis for this conclusion, 26 additional bis(propargyloxy) disulfides were prepared (see Table 1 for the total of 36 examples), and their diverse reactions monitored. It was found that the bis(propargyloxy) disulfides may be divided into the classes detailed below on the basis of the products they yield.




15 16

**Scheme 2**

**Table 1** Preparation of Bis(propargyloxy) Disulfides (Scheme 1)

| Entry | Alcohol | Bis(propargyloxy) disulfide | $R^1$ | $R^2$ | $R^3$ | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | **1** | **8**[7a,c] | H | H | H | 98 |
| 2 | **2a** | **9a** | Me | H | H | 98 |
| 3 | **2b** | **9b** | Et | H | H | 72 |
| 4 | **2c** | **9c** | $(CH_2)_4Me$ | H | H | 61 |
| 5 | **2d** | **9d** | *i*-Pr | H | H | 87 |
| 6 | **2e** | **9e** | *i*-Bu | H | H | 91 |
| 7 | **2f** | **9f** | $CH_2$-*t*-Bu | H | H | 89 |
| 8 | **2g** | **9g** | tetrahydro-3-furyl | H | H | 93 |
| 9 | **2h** | **9h** | $CHPh_2$ | H | H | 91 |
| 10 | **3a** | **10a** | H | H | Me | 98 |
| 11 | **3b** | **10b** | H | H | Et | 85 |
| 12 | **3c** | **10c** | H | H | $CMe=CH_2$ | 98 |
| 13 | **3d** | **10d**[7a,c] | H | H | Ph | 91 |
| 14 | **3e** | **10e** | H | H | $CH_2OTBDMS$ | 92 |
| 15 | **3f** | **10f** | H | H | TMS | 86 |
| 16 | **3g** | **10g** | H | H | TBDMS | 94 |
| 17 | **3h** | **10h** | H | H | *t*-Bu | 98 |
| 18 | **4a** | **11a** | H | H | cyclohexen-1-yl | 98 |
| 19 | **4b** | **11b** | Me | H | Ph | 81 |
| 20 | **4c** | **11c** | H | H | $CH_2OTHP$ | 98 |
| 21 | **4d** | **11d** | Me | H | $CH_2OTHP$ | 87 |
| 22 | **4e** | **11e** | $CHPh_2$ | H | Ph | 88 |
| 23 | **4f** | **11f** | H | H | Br | 87 |
| 24 | **4g** | **11g** | H | H | $CH_2SO_2Ph$ | 81 |
| 25 | **4h** | **11h** | *t*-Bu | H | Ph | 93 |
| 26 | **4i** | **11i** | H | H | TBDPS | 95 |
| 27 | **4j** | **11j** | H | H | 1-Naph | 95 |
| 28 | **5a** | **12a** | *t*-Bu | H | H | 83 |
| 29 | **5b** | **12b** | $CMe_2CH_2CH=CH_2$ | H | H | 93 |

**Table 1** Preparation of Bis(propargyloxy) Disulfides (Scheme 1) (continued)

| Entry | Alcohol | Bis(propargyloxy) disulfide | $R^1$ | $R^2$ | $R^3$ | Yield (%) |
|---|---|---|---|---|---|---|
| 30 | **5c** | **12c** | $CMe_2CH_2Cl$ | H | H | 88 |
| 31 | **5d** | **12d** | $CMe_2CH_2Br$ | H | H | 85 |
| 32 | **5e** | **12e** | adamantyl | H | H | 84 |
| 33 | **5f** | **12f** | $CBr_3$ | H | H | 44 |
| 34 | **5g** | **12g** | Cy | H | H | 81 |
| 35 | **6** | **13** | Ph | H | H | 41 |
| 36 | **7** | **14**[a] | Me | Me | H | – |

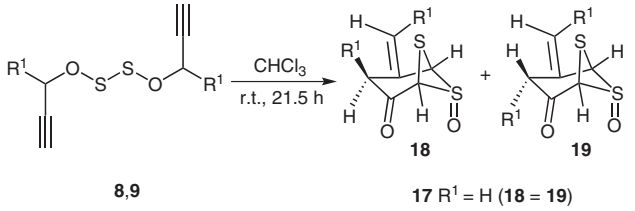
[a] Compound **14** was prepared by a modified procedure (see Scheme 8 and the discussion below) and not isolated due to its high reactivity.

The unsubstituted bis(propargyloxy) disulfide (**8**) and the α,α′-substituted bis(propargyloxy) disulfides **9a–c**,**e–h**[9] in which the substituent is an acyclic primary or secondary alkyl group, underwent rearrangement at room temperature in chloroform solution, yielding novel 6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxide derivatives, which are structurally related to the biologically active zwiebelanes, isolated from freshly cut onion by Block.[10] Unsubstituted bis(propargyloxy) disulfide **8** produced dithiabicyclic compound **17**[7a,c] as a single product (Scheme 3, Table 2). However, in the case of α-substituted bis(propargyloxy) disulfides (**9a–c**,**e–h**[9]), a mixture of two isomers was obtained (**18a–c**,**e–h**, **19a–c**,**e–h**, Scheme 3, Table 2).[7a,c] There are three possible explanations for the formation of two isomers. The first one is that these are two stereoisomers of the sulfoxide function (*exo*/*endo*). We discarded this possibility, as this would not explain the formation of a single product **17** from **8** . In addition, the bridgehead protons and carbon atoms are very similar in these two isomers. The second possible explanation is that these are *Z*/*E* isomers of the double bond. In fact, we suggested this in our original communication.[7a] However, in view of the observation of one of the referees to this paper, we carefully repeated a full NMR analysis for the mixture of isomers **18b** and **19b** ($R^1$ = Et), including three 2D techniques (NOESY, HMQC, and HMBC), on our 16.4 T instrument (700.5 and 176.1 MHz for $^1H$ and $^{13}C$, respectively). It turns out that in both isomers there is a strong NOE interaction between the allylic methylene protons and one of the bridgehead protons. Conversely, in both isomers there is a strong NOE interaction between the olefinic proton and at least one of the methylene protons of the other ethyl group. This constitutes definite proof that in both isomers the double bond has *Z* stereochemistry. The third possible explanation is that these are stereoisomers on the chiral carbon atom C-3 a to the carbonyl group. This is supported by the fact that the chemical shifts of the hydrogen atoms at this site (H-3) are very different for each isomer (e.g., δ = 4.00 for **18b** and δ = 3.24 for **19b**), while the chemical shifts of all the other hydrogen atoms are very similar. In addition, the allylic coupling between this hydrogen (H-3) and the olefinic proton are also different (2.5 and 1.5 Hz, respectively), indicating that the former is closer to perpendicular to the plane of the double bond – and indeed the NOE interaction between the olefinic proton and H-3 is ca. four times weaker in the former relative to the latter.

The *R*- and *S*-configurations on the C-3 of two diastereomers were assigned on the basis of the strong deshielding of H-3 by the sulfoxide function in the *endo* position of the diastereomer **18b** (δ = 4.00 ppm), relative to the diastereomer **19b** (δ = 3.24 ppm). The same influence of the *endo*-sulfoxide function is seen in one of the proton atoms of

**Table 2** Rearrangement of α,α′-Substituted Bis(propargyloxy) Disulfides (Scheme 3)

| Entry | Bis(propargyloxy) disulfide | $R^1$ | Product | Ratio **18**/**19** | Total yield (**18** + **19**) (%) |
|---|---|---|---|---|---|
| 1 | **8** | H | **17**[7a,c] | – | 69 |
| 2 | **9a** | Me | **18a**,[7a,c] **19a**[7a,c] | 4.7:1.0 | 39 |
| 3 | **9b** | Et | **18b**, **19b** | 2.0:1.0 | 29 |
| 4 | **9c** | $(CH_2)_4Me$ | **18c**, **19c** | 1.6:1.0 | 29 |
| 5 | **9e** | *i*-Bu | **18e**, **19e** | 1.8:1.0 | 63 |
| 6 | **9f** | $CH_2$-*t*-Bu | **18f**, **19f** | 2.5:1.0 | 32 |
| 7 | **9g** | tetrahydro-3-furyl | **18g**, **19g** | 1.2:1.0 | 63 |
| 8 | **9h** | $CHPh_2$ | **18h**, **19h** | 2.75:1.0 | 62 |



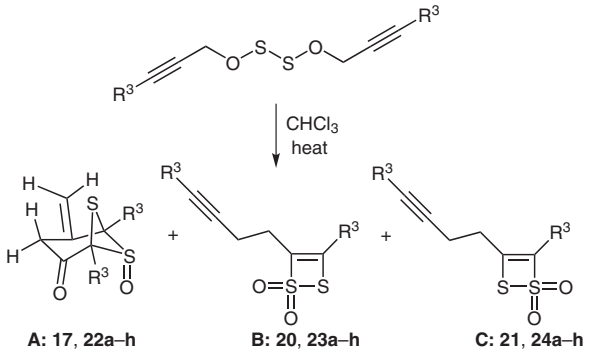

**Scheme 3**

the 3-methylene in the unsubstituted derivative **17** (δ = 3.86 against 3.49 ppm) and is consistent with the $^1$H NMR spectral data for the analogous 2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane reported by Block.[10b] The 3*S*,5*S*,6*S*,*Z*-diastereomer **18** was the major product and the 3*R*,5*S*,6*S*,*Z*-diastereomer **19** was the minor product in all cases (Table 2).

On the basis of the spectral data described above, we propose that the stereochemistry of the sulfoxide function in compounds **17** and **18/19** has an *endo* conformation, which is also presumed to be the more stable one in these cases as a result of the possible overlap of a bridge-sulfur lone pair and the sulfoxide σ* orbitals.

The nature of the substituent at C-α of the propargyl moieties significantly affected the ratio of isolated products. Sterically demanding substituents at this position decrease the ratio of **18** to **19**. In the case of a methyl-substituted derivative the ratio **18a/19a** was 4.7:1, in the case of a tetrahydrofuryl-substituted derivative the ratio **18g/19g** decreased to 1.2:1.

As noted above, the γ,γ′-substituted bis(propargyloxy) disulfides proved to be significantly more stable than their α,α′-substituted counterparts. However, heating in refluxing chloroform solution led to a mixture of a 6,7-dithiabicyclo[3.1.1]heptan-2-one 6-oxide (**A**) and two isomeric product types, **B** and **C** (Scheme 4, Table 3).[7a,d] The latter can be distinguished by comparing the chemical shifts of the olefinic carbon atoms C-1 and C-2. Substitution at C-γ of the propargylic moieties significantly improved the total isolated yields and its nature affected the ratio of products (Table 3). Large silyl substituents at this position slowed the reaction (**10g**, $R^3$ = TBDMS, 7 d, 83% yield vs. unsubstituted bis(propargyloxy) disulfide **8**, 7 h, 49% yield). A γ-*tert*-butyl substituent (**10h**) resulted in quantitative conversion. Bulky substituents increased the ratio of **B** to **C**, presumably as a result of the interaction between $R^3$ and the sulfone group in **C**, and decrease the amount of **A** (cf. **10f**, **10g**, and **10h**, Table 3). Although compounds with a saturated four-membered ring thiosulfonate function have been reported previously[10a,11] (as the products of dimerization of sulfines followed by intramolecular disproportionation), the α,β-unsaturated four-membered cyclic thiosulfonate grouping present in products **B** and **C** appears to have been unknown to date.



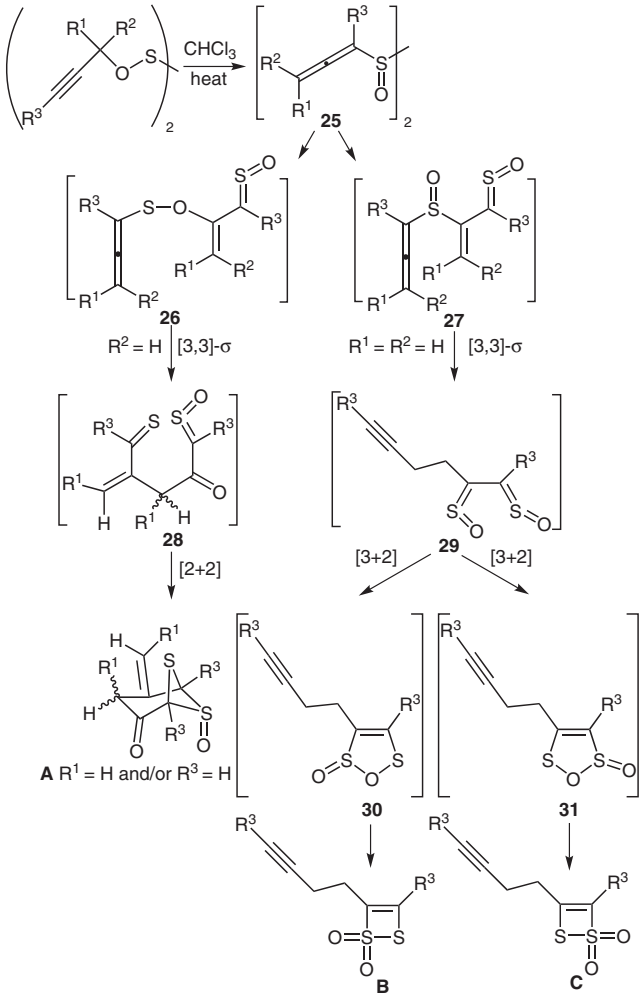

**Scheme 4**

In surprising contrast to the findings noted above, compounds **11a**–**j** (Table 1) did not undergo rearrangement under the stated conditions. Although it is tempting to attribute this finding to steric effects of the α,α′/γ,γ′ substituent groups, in the absence of supporting evidence we refrain from offering a rationalization.

An outline of the reaction paths is presented in Scheme 5.[7d] First, [2,3]-sigmatropic rearrangement on each side of the molecule converts the bis(propargyloxy) disulfide into an α-disulfoxide **25**, which dissociates into two allenesulfinyl radicals.[8a] Recombination of two such radicals, via the sulfinyl oxygen of one and C-2 of the other, gives **26**, while recombination via the sulfinyl sulfur of

**Table 3** Rearrangement of γ,γ′-Substituted Bis(propargyloxy) Disulfides (Scheme 4)

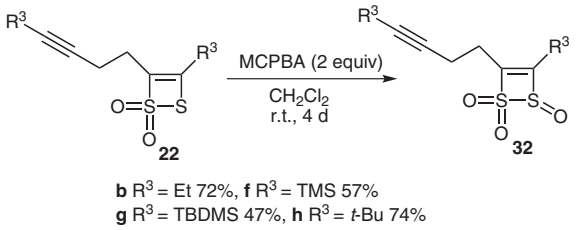
| Entry | Bis(propargyloxy) disulfide | $R^3$ | Time | Products **A/B/C** | Products ratio | Total yield (%) |
|---|---|---|---|---|---|---|
| 1 | **8** | H | 7 h | **17/20**[7a,d]**/21**[7a,d] | 2.26:0.22:1.00 | 49 |
| 2 | **10a** | Me | 10 h | **22a/23a/24a** | 0.23:1.01:1.00 | 69 |
| 3 | **10b** | Et | 7.5 h | **22b/23b**[7a,d]**/24b**[7a,d] | 0.29:1.20:1.00 | 85 |
| 4 | **10c** | $CMe=CH_2$ | 11.5 h | **22c/23c/24c** | 1.45:1.17:1.00 | 82 |
| 5 | **10d** | Ph | 14 h | **22d/23d/24d** | 0.57:0.74:1.00 | 63 |
| 6 | **10e** | $CH_2OTBDMS$ | 7 h | **22e/23e/24e** | 0.93:0.99:1.00 | 61 |
| 7 | **10f** | TMS | 20 h | **23f**[7a,d]**/24f**[7a,d] (no **22f**) | 2.98:1.00 | 76 |
| 8 | **10g** | TBDMS | 161 h (~7 d) | **23g/24g** (no **22g**) | 3.65:1.00 | 83 |
| 9 | **10h** | *t*-Bu | 25 h | **22h/23h**[7a,d] (no **24h**) | 1.00:11.20 | 100 |




Scheme 5

one and C-2 of the other yields **27**. The [3,3]-sigmatropic rearrangement of **26** followed by a head-to-tail intramolecular [2+2] cycloaddition of the intermediate sulfine and thioaldehyde functions (**28**) leads to **A**. A [3,3]-sigmatropic rearrangement of **27** to *vic*-disulfine **29** followed by electrocyclic ring closure to **30/31**, and then intramolecular disproportionation, leads to **B** and **C**.

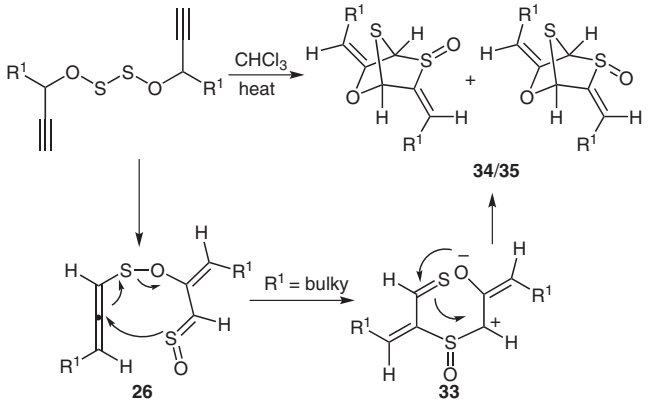
Oxidation of the new cyclic thiosulfonate of type **B** with two equivalents of *m*-chloroperoxybenzoic acid in dichloromethane afforded a sulfinyl sulfone product **32**, but no disulfone was observed (Scheme 6).




**b** $R^3$ = Et 72%, **f** $R^3$ = TMS 57%
**g** $R^3$ = TBDMS 47%, **h** $R^3$ = *t*-Bu 74%

Scheme 6

The versatility of the system under study is demonstrated by the behavior of **12a–e**, bearing sterically demanding substituents at C-α. Following reflux of chloroform solutions of each of these bis(propargyloxy) disulfides **12a–e** (the reactions were characterized by a deep red solution), a series of two new isomeric dithiabicyclic products **34a–e/35a–e** was isolated (Scheme 7, Table 4). Heating overnight in chloroform solution led to interconversion of the isomers, presumably by an unusually rapid pyramidal inversion of the sulfoxide function.[12] Each isomer separately led to the same equilibrium mixture (Table 4).




Scheme 7

A kinetic study by NMR spectroscopy of the interconversion **34a→35a** established that the inversion barrier, Δ*G*, in chloroform-*d* solution at 47 °C was 24.70 kcal/mol, with $t_{1/2}$ = 30.06 hours, and 25.07 kcal/mol in benzene-$d_6$ solution, with $t_{1/2}$ = 3.76 hours. These barriers to sulfoxide inversion in **34a/35a** are much lower than these for simple aliphatic sulfoxides (e.g. Δ*G* = 40 kcal/mol for dimethyl sulfoxide) and much larger than that for aromatic hetero-

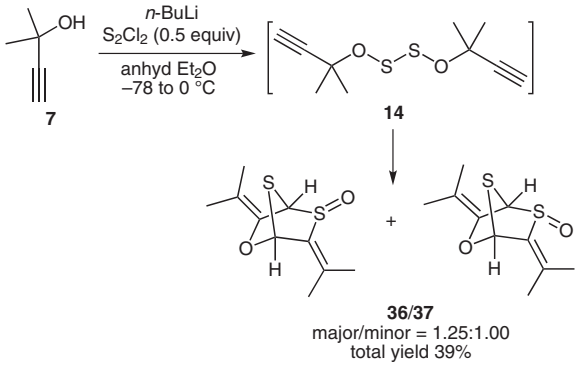
**Table 4** Rearrangement of α,α′-*tert*-Alkyl-Substituted Bis(propargyloxy) Disulfides (Scheme 7)

| Entry | Bis(propargyloxy) disulfide | $R^1$ | Products | Ratio **34/35** | Time | Total yield (%) |
|---|---|---|---|---|---|---|
| 1 | **12a** | *t*-Bu | **34a**[7a,d]/**35a**[7a,d] | 2.51:1.00 | 1.5 h | 57 |
| 2 | **12b** | $CMe_2CH_2CH=CH_2$ | **34b/35b** | 2.99:1.00 | 1.5 h | 53 |
| 3 | **12c** | $CMe_2CH_2Cl$ | **34c/35c**[a] | 2.08:1.00 | 1 h 50 min | 74 |
| 4 | **12d** | $CMe_2CH_2Br$ | **34d/35d** | 2.02:1.00 | 1.5 h | 66 |
| 5 | **12e** | adamantyl | **34e**[7a,d]/**35e**[7a,d] | 3.34:1.00 | 2 h | 62 |

[a] This reaction was also carried out at r.t. After 2 d, only the major product was obtained in 24% yield.

cyclic sulfoxides (e.g. $\Delta G$ = 14.8 kcal/mol for thiophene-1-oxide).[13] Bis(propargyloxy) disulfides **12f** and **12g** (Scheme 1, Table 1) did not undergo rearrangement under the stated conditions. Dithiabicyclic structures **34/35** can be formed from the same intermediate **26** from Scheme 5, but by a different path[7d] (Scheme 7), probably because of initial allylic steric interaction of the bulky substituents at the point of the [3,3]-sigmatropic rearrangement of **26**.

Substitution at C-α, especially with sterically demanding groups, lower stability as well as the yield of bis(propargyloxy) disulfides. Although the synthesis of di-*tert*-butoxy disulfide was recently reported,[2a] no yield was noted. Considerable effort was invested to obtain bis(propargyloxy) disulfides derived from tertiary propargylic alcohols which were expected to be extremely unstable. The procedure used for primary and secondary bis(propargyloxy) disulfides failed even at low temperature and with different tertiary amine bases. Only upon reaction of α,α-dimethylpropargyl alcohol, *n*-butyllithium, and sulfur monochloride at –78 °C was product in the form of 2-oxa-5,7-dithiabicyclo[2.2.1]heptane 5-oxide derivatives obtained (Scheme 8). The intermediate bis(α,α-dimethylpropargyloxy) disulfide could not be isolated. When the reaction mixture was warmed to 0 °C, the solution turned to deep red in color. Careful workup led to isolation of 3,6-bis(1-methylethylidene)-2-oxa-5,7-dithiabicyclo[2.2.1]heptane 5-oxide (corresponding to the minor isomer of structures **34/35**), which after a few hours in chloroform solution at room temperature converted into a mixture of the two isomers **36/37** by unusually rapid sulfoxide inversion (Scheme 8). Starting with other tertiary alcohols, such as 1-ethynylcyclohexanol and 3,4-dimethylpent-1-yn-3-ol, led to the same type of products as **36/37**. They were identified as crude products, but due to their instability could not be isolated.




**Scheme 8**

The reactivity of a variety of bis(propargyloxy) disulfides has been studied. The product type and the rearrangement paths leading to them have been found to be dependent upon the α/γ substitution pattern as shown in Schemes 4 and 7. Three novel types of products were discovered: dithiabicyclic structures **A**, which are structurally related to the biologically active zwiebelanes, α,β-unsaturated four-membered cyclic thiosulfonates **B/C**, and dithiabicyclic structures **34/35** and **36/37**. The remarkable sequence of sigmatropic rearrangements and cycloadditions involved in their formation constitutes surprising organosulfur chemistry of synthetic and mechanistic interest.

$Et_2O$ was dried over Na. THF was distilled from Na/benzophenone. $S_2Cl_2$ was distilled from sulfur and activated carbon. All other solvents and reagents were commercially available and were used without further purification. Alcohols **1**, **2a–c**, **3a**,**b**,**f**, **6a**, and **7** were commercially available. Alcohols **2d** (67%), **2e** (47%), **2f** (67%), **2g** (50%), **2h** (88%), **5a** (76%), **5b** (99%), **5c** (72%), **5d** (81%), **5e** (59%), **5f** (38%), and **5g** (85%) were prepared from ethynylmagnesium bromide and the corresponding aldehyde in anhyd THF (1 h, 0 °C; 1 h, r.t.). Aldehydes for the preparation of alcohols **5c–e** were obtained by oxidation of the commercially available appropriate alcohols with PCC in $CH_2Cl_2$ at r.t. for 2 h in yields of 67, 84, and 95%, respectively. Alcohols **3c** (100%), **3d** (100%), **3e** (95%), **3h** (97%), **4a** (81%), **4b** (100%), **4c** (44%), **4d** (95%), **4e** (100%), **4h** (84%) were prepared from the corresponding acetylene and aldehyde, using TMEDA and *n*-BuLi, in anhyd THF (–78 °C, 30 min, then r.t., 1.5 h). Alcohol **3g** was prepared from THP-protected unsubstituted propargylic alcohol [2-(prop-2-ynyloxy)tetrahydro-2*H*-pyran] with TBDMSCl, TMEDA, and *n*-BuLi in anhyd THF (–78 °C, 30 min, then r.t., 1.5 h, 98%), followed by deprotection with CSA in refluxing EtOH overnight (98%). Alcohol **4g** was prepared from (prop-2-ynylsulfanyl)benzene and paraformaldehyde, by using TMEDA and *n*-BuLi, in anhyd THF (30 min, –78 °C; 1.5 h, r.t., 63%), followed by oxidation with MCPBA in $CH_2Cl_2$ (72%). Alcohol **4f** was obtained from reaction of unsubstituted propargylic alcohol with $Br_2$ in $H_2O$ and by using an excess of KOH (5 °C, 45 min, 56%). Alcohol **4i** was prepared from the reaction of 2-(prop-2-ynyloxy)tetrahydro-2*H*-pyran with TBDPSCl, TMEDA, and *n*-BuLi in anhyd THF (–78 °C, 30 min, then r.t., 1.5 h), followed, without further isolation, by deprotection with CSA in refluxing EtOH overnight (17% for both steps). Alcohol **4j** was obtained from the coupling of 1-bromonaphthalene and 2-(prop-2-ynyloxy)tetrahydro-2*H*-pyran, by using dichlorobis(triphenylphosphine)palladium(II), DBU, and CuI (anhyd toluene, reflux, 2 h, 100%), followed by deprotection with CSA in refluxing EtOH overnight (28%). Column chromatography was performed on silica gel 60 (230–400 mesh), and TLC was run on precoated Merck silica gel plates 60 $F_{254}$ (2.00 mm). Melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet 60 SXB FTIR instrument. High-resolution mass spectra were obtained on a VG-Fison Autospec instrument. NMR spectra were recorded at 298 K on 200, 300, or 600 MHz spectrometers ($^{13}C$: 50, 75, or 150 MHz, respectively) of samples dissolved in either $CDCl_3$ or other deuterated solvents, and by using $SiMe_4$ as internal standard. In some cases the structures were unambiguously determined with the aid of two-dimensional techniques such as COSY, HMQC, and HMBC. The stereochemistry of the double bonds was assigned using the NOESY technique.

**Bis(propargyloxy) Disulfides; General Procedure**

To a stirred soln of the appropriate alcohol (10 mmol) and $Et_3N$ (10 mmol) in $Et_2O$ (100 mL) at 0 °C, a soln of $S_2Cl_2$ (5 mmol) in $Et_2O$ (50 mL) was added dropwise. The $Et_3N{\cdot}HCl$ salt precipitated as a white solid. After stirring of the reaction mixture for 1 h, the salt was filtered under vacuum and the $Et_2O$ soln was washed with ice water. Drying ($MgSO_4$) and removal of the solvent under reduced pressure were carried out with external cooling. *To prevent local exposure, the cold solvent required for the next step was added immediately after evaporation.*

**Bis[(1-methylprop-2-ynyl)oxy] Disulfide (9a)**
Yellow liquid; strong smell of garlic; mixture of four diastereomers; yield: 98%.

IR (neat): 1020, 1325, 1374, 2118, 2252, 2990, 3305 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): δ = 4.68, 4.66, 4.65, and 4.63 (qd, *J* = 6.6, 2.1 Hz, 2 H each), 2.60, 2.59, 2.554, 2.550 (d, *J* = 2.1 Hz, 2 H each), 1.56, 1.55, 1.54, and 1.53 (d, *J* = 6.6 Hz, 6 H each).

$^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 82.74 and 82.67 (≡C– each), 82.6 (≡C– for two isomers), 75.2, 75.1, 74.8 and 74.7 (≡CH each), 71.1, 71.1, 69.23 and 69.21 (–CH–O each), 22.6, 22.5, 22.4 and 22.3 ($–CH_3$ each).

MS (CI, $CH_4$): *m*/*z* (%) = 203 (23) [$MH^+$], 154 (27) [$M^+$ – 'SO'], 101 (100) [$M^+$/2].

HRMS: *m*/*z* [$MH^+$] calcd for $C_8H_{11}O_2S_2$: 203.0200; found: 203.0197.

**Bis(but-2-ynyloxy) Disulfide (10a)**
Yellow liquid; strong smell of garlic; yield: 98%.

IR (neat): 928, 1148, 1358, 1439, 1608, 2235, 2918 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): δ (AB system) = 4.47 and 4.40 (dq, *J* = 14.7, 2.4 Hz, 2 H), 1.88 (t, *J* = 2.4 Hz, 6 H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 84.9 (≡C–), 74.2 (≡C–), 62.2 ($–CH_2–$), 3.8 ($–CH_3$).

MS (CI, $CH_4$): *m*/*z* (%) = 203 (48) [$MH^+$], 189 (100) [$C_9H_7O_2S_2$], 171 (33) [$MH^+$ – 'S'], 153 (85).

HRMS: *m*/*z* [$MH^+$] calcd for $C_8H_{11}O_2S_2$: 203.0200; found: 203.0203.

**Bis[(1-methyl-3-phenylprop-2-ynyl)oxy] Disulfide (11b)**
Yellow liquid; mixture of four diastereomers; yield: 81%.

IR (neat): 1018, 1079, 1330, 1490, 2250, 2986 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.47–7.40 (m, 4 H for four isomers), 7.31–7.27 (m, 6 H for four isomers), 4.93, 4.90, 4.870, and 4.866 (q, *J* = 6.7 Hz, 2 H each), 1.62 and 1.61 (d, *J* = 6.7 Hz, 6 H each), 1.60 (d, *J* = 6.7 Hz, 6 H for two isomers).

$^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 134.9, 131.8, 128.7, 128.6, 128.4, 128.3, and 122.4 (Ar for four isomers), 88.14 and 88.09 (≡C− each), 88.0 (≡C− for two isomers); 86.9 (≡C− for two isomers), 86.7 and 86.6 (≡C− each); 72.0 (−CH− for two isomers), 70.12 and 70.08 (−CH− each), 22.7, 22.62, 22.55, and 22.5 ($−CH_3$ each).

MS (CI, $CH_4$): *m*/*z* (%) = 355 (11) [$MH^+$], 323 (19) [$MH^+$ – 'S'], 307 (13) [$MH^+$ – 'SO'], 291 (17) [$MH^+$ – '$SO_2$'], 275 (14) [$MH^+$ – '$S_2O$'], 177 (11) [$M^+$/2], 129 (100).

HRMS: *m*/*z* [$MH^+$] calcd for $C_{20}H_{19}O_2S_2$: 355.0826; found: 355.0841.

**Bis[(1-*tert*-butylprop-2-ynyl)oxy] Disulfide (12a)**
Yellow liquid; mixture of four diastereomers; yield: 83%.

IR (neat): 1129, 1216, 1366, 1477, 1950, 2121, 2966, 3304 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): δ = 4.188, 4.140, 4.138, and 4.132 (d, *J* = 2.1 Hz, 2 H each), 2.58, 2.55, 2.51, and 2.50 (d, *J* = 2.1 Hz, 2 H each), 1.033 and 1.015 (s, 18 H each), 1.019 (s, 18 H for two isomers).

$^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 85.3, 85.0, 81.8, and 81.7 (−CH−O each), 81.0 and 80.9 (≡C– each), 80.6 (≡C– for two isomers); 76.6, 76.3, 75.7, and 75.6 (≡CH each), 36.3, 36.2, 36.0, and 35.9 [$−C(CH_3)_3$ each], 25.8, 25.74, 25.67 and 25.6 [$−C(CH_3)_3$ each].

MS (CI, $CH_4$): *m*/*z* (%) = 286 (42) [$M^+$], 254 (33) [$M^+$ –'S'], 159 (100).

HRMS: *m*/*z* [$M^+$] calcd for $C_{14}H_{22}O_2S_2$: 286.1061; found: 286.1059.

**Rearrangement of α-Alkyl-Substituted Bis(propargyloxy) Disulfides; General Procedure**
Unless otherwise specified, a $CHCl_3$ soln of the appropriate bis(propargyloxy) disulfide was stirred at r.t. for 21.5 h.[14] This reaction was characterized by the soln turning dark brown in color. The solvent was evaporated under reduced pressure and the residue was purified by chromatography (silica gel).

**(3*S*,5*S*,6*S*,*Z*)- and (3*R*,5*S*,6*S*,*Z*)-3-Isobutyl-4-(3-methylbutylidene)-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-Oxide (18e and 19e)**
A $CHCl_3$ soln of the reactant was heated at reflux for 5 min and the product was obtained as a mixture of two diastereomers **18e** and **19e** (1.8:1.0) as a yellow liquid, upon chromatography (silica gel, *n*-hexane–EtOAc, 100:1→200:5→95:5→8:1→4:1); total yield: 63%.

IR (neat): 1114 (S=O), 1714 (C=O) $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): δ = 5.97 [td, *J* = 7.8, 2.3 Hz, 1 H (=CH–) for **18e**] and 5.92 [td, *J* = 7.8, 1.0 Hz, 1 H (=CH–) for **19e**], 5.49 [d, *J* = 5.1 Hz, 1 H (CH–C=) for **18e**] and 5.42 [d, *J* = 5.0 Hz, 1 H (CH–C=) for **19e**], 4.56 ]d, *J* = 5.1 Hz, 1 H (CH–C=O) for **18e**] and 4.52 [d, *J* = 5.0 Hz, 1 H (CH–C=O) for **19e**], 4.07 [tm, *J* = 6.0 Hz, 1 H (CH–*i*-Bu) for **18e**] and 3.32 [tm, *J* = 6.8 Hz, 1 H (CH–*i*-Bu) for **19e**], 2.12–1.98 (m, 4 H for both diastereomers), 1.88 (sept, *J* = 7.8 Hz, 1 H for **19e**) and 1.87 (sept, *J* = 7.8 Hz, 1 H for **18e**), 1.703 (sept, *J* = 7.8 Hz, 1 H for **18e**) and 1.698 (sept, *J* = 7.8 Hz, 1 H for **19e**), 0.97 (d, *J* = 7.8 Hz, 12 H for **18e**), 0.93 (d, *J* = 7.8 Hz, 6 H for **19e**), 0.92 (d, *J* = 7.8 Hz, 6 H for **19e**).

$^{13}C$ NMR (150 MHz, $CDCl_3$): δ = 201.5 (C=O for **18e**) and 200.9 (C=O for **19e**), 136.5 (=CH– for **19e**) and 134.3 (=CH– for **18e**), 128.1 (=C– for **19e**) and 127.5 (=C– for **18e**), 69.3 (CH–C=O for **18e**) and 67.6 (CH–C=O for **19e**), 67.4 (CH–C= for **18e**) and 65.3 (CH–C= for **19e**), 51.0 (–CH–*i*-Bu for **19e**) and 49.5 (–CH–*i*-Bu for **18e**), 37.1 ($–CH_2–$ for **18e**) and 36.9 ($–CH_2–$ for **19e**), 34.5 ($–CH_2–$ for both diastereomers), 28.9 [$–CH(CH_3)_2$ for **18e**] and 28.8 [$–CH(CH_3)_2$ for **19e**], 26.4 [$–CH(CH_3)_2$ for **18e**] and 25.8 [$–CH(CH_3)_2$ for **19e**], 22.9 ($–CH_3$ for **18e**), 22.52 [$–CH_3$ (×2) for **18e**], 22.51 ($–CH_3$ for **19e**), 22.44 ($–CH_3$ for **19e**), 22.41 ($–CH_3$ for **19e**), 22.4 ($–CH_3$ for **19e**), 22.3 ($–CH_3$ for **18e**).

MS (CI, $CH_4$): *m*/*z* (%) = 287 (15) [$MH^+$], 253 (17) [$(M – H)^+$ – 'S'], 237 (21) [$(M – H)^+$ – 'SO'].

HRMS: *m*/*z* [$MH^+$] calcd for $C_{14}H_{23}O_2S_2$: 287.1139; found: 287.1135.

**Rearrangement of γ,γ′-Alkyl-Substituted Bis(propargyloxy) Disulfides; General Procedure**
A $CHCl_3$ soln of the appropriate bis(propargyloxy) disulfide was heated under reflux for the time indicated in Table 3. This reaction was characterized by the soln turning a darker color. After the mixture had cooled to r.t., the solvent was evaporated under reduced pressure and the residue was purified by chromatography (silica gel, *n*-hexane–$CHCl_3$, 1:1→1:2→1:3→0:1).

**(5*S*,6*S*)-1,5-Dimethyl-4-methylene-6,7-dithiabicyclo[3.1.1]heptan-2-one 6-Oxide (22a)**
IR (neat): 1098 (S=O), 1715 (C=O) $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): δ = 5.40 [t, *J* = 1.5 Hz, 1 H of $=CH_2$ (*cis* to $−CH_2−$)], 5.32 [t, *J* = 2.0 Hz, 1 H of $=CH_2$ (*trans* to $−CH_2−$)], AB system: 3.88 (dt, $J_{gem}$ = 20.5, *J* = 2.0 Hz, 1 H) and 3.50 (dt, $J_{gem}$ = 20.5, *J* = 1.5 Hz, 1 H), 1.98 [s, 3 H ($CH_3$−CH−C=)], 1.78 [s, 3 H ($CH_3$−CH−C=O)].

$^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 198.8 (C=O), 138.6 (=C−), 116.9 ($=CH_2$), 74.50 (−C−C=O), 73.6 (−C−C=), 42.7 ($−CH_2−$), 21.2 ($−CH_3$), 16.8 ($−CH_3$).

MS (CI, $CH_4$): *m/z* (%) = 203 (88) [$MH^+$], 171 (7) [$MH^+$ – 'S'], 155 (25) [$MH^+$ – 'SO'], 154 (100) [$M^+$ – 'SO'].

HRMS: *m/z* [$MH^+$] calcd for $C_8H_{11}O_2S_2$: 203.0200; found: 203.0193.

**Oxidation of 1,2-Dithiete 1,1-Dioxide to 1,2-Dithiete 1,1,2-Trioxide; General Procedure**

A soln of MCPBA (10 mmol) in $CH_2Cl_2$ (20 mL) was added dropwise to a cooled (–40 °C), stirring soln of the appropriate 1,2-dithiete 1,1-dioxide (5 mmol) in $CH_2Cl_2$ (20 mL). Then the reaction mixture was warmed to r.t. and stirred for 4 d. The $CH_2Cl_2$ soln was washed with aq KI/$Na_2S_2O_3$ (3 × 10 mL), $NaHCO_3$ (3 × 10 mL), and then $H_2O$ (10 mL). After drying ($MgSO_4$) of the soln and removal of the solvent, the products were isolated after chromatography (silica gel).

**3-Ethyl-4-hex-3-ynyl-1,2-dithiete 1,1,2-Trioxide (32b)**

Yellow liquid; chromatography (silica gel, *n*-hexane–EtOAc, 1:0→95:5→8:1→4:1); yield: 72%.

IR (neat): 1134, 1160, 1319, 1460, 1643, 1726, 2360, 2976 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): see Figure 1 and Table 5.

$^{13}C$ NMR (75 MHz, $CDCl_3$): see Figure 1 and Table 6.

MS (EI): *m/z* (%) = 246 (70) [$M^+$], 183 (53) [$MH^+$ – '$SO_2$'], 167 (89) [($MH^+$ – '$SO_2$' – 'O'], 105 (100).

HRMS: *m/z* [$M^+$] calcd for $C_{10}H_{15}O_3S_2$: 246.0384; found: 246.0402.

**3-(Trimethylsilyl)-4-[4-(trimethylsilyl)but-3-ynyl]-1,2-dithiete 1,1,2-Trioxide (32f)**

Yellow liquid; chromatography (silica gel, $CHCl_3$); yield: 57%.

IR (neat): 1137, 1159, 1251, 1369, 1592, 1728, 2177, 2959 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): see Figure 1 and Table 5.

$^{13}C$ NMR (75 MHz, $CDCl_3$): see Figure 1 and Table 6.

MS (EI): *m/z* (%) = 335 (11) [$MH^+$], 270 (75) [$M^+$ – '$SO_2$'], 255 (26) [$MH^+$ – '$SO_2$' – 'O'], 207 (100).

HRMS: *m/z* [$MH^+$] calcd for $C_{12}H_{23}O_3Si_2S_2$: 335.0627; found: 335.0624.

**3-(*tert*-Butyldimethylsilyl)-4-[4-(*tert*-butyldimethylsilyl)but-3-ynyl]-1,2-dithiete 1,1,2-Trioxide (32g)**

Yellow liquid; yield: 47%.

IR (neat): 1042, 1251, 1359, 1471, 1716, 2178, 2929 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): see Figure 1 and Table 5.

$^{13}C$ NMR (75 MHz, $CDCl_3$): see Figure 1 and Table 6.

MS (EI): *m/z* (%) = 419 [$MH^+$], 339 (6) [$MH^+$ – '$SO_2$' – 'O'], 113 (100).

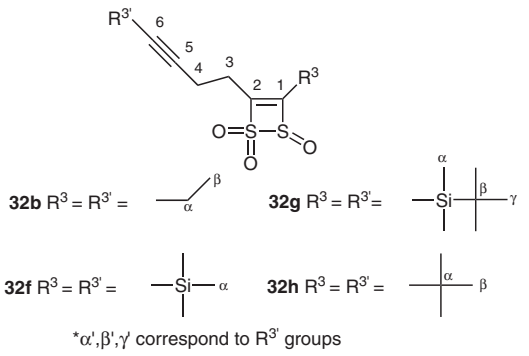



**Figure 1**

HRMS: *m/z* [$MH^+$] calcd for $C_{18}H_{35}O_3Si_2S_2$: 419.1566; found: 419.1555.

**3-*tert*-Butyl-4-(5,5-dimethylhex-3-ynyl)-1,2-dithiete 1,1,2-Trioxide (32h)**

Yellow liquid; chromatography (silica gel, *n*-hexane–EtOAc, 4:1); yield: 74%.

IR (neat): 1142, 1162, 1267, 1367, 1475, 1611, 1646, 2247, 2969 $cm^{-1}$.

$^1H$ NMR (600 MHz, $CDCl_3$): see Figure 1 and Table 5.

**Table 5** $^1H$ NMR Chemical Shifts (δ) for 1,2-Dithiete 1,1,2-Trioxides **32**[a]

| H | 32b | 32f | 32g | 32h |
|---|---|---|---|---|
| 3 | 2.81 | 3.01/2.94 | 3.02 | 3.11/2.88 |
| 4 | 2.58/2.48 | 2.70/2.56 | 2.76/2.61 | 2.64/2.50 |
| α | 2.70 | 0.46 | 0.11[b] | |
| β | 1.33 | | | 1.50 |
| γ | | | 1.01 | |
| α′ | 2.15 | 0.15 | 0.10[b] | |
| β′ | 1.11 | | | 1.19 |
| γ′ | | | 0.89 | |

[a] $^1H$ NMR spectra (600 MHz) of samples in $CDCl_3$ with TMS as internal reference were obtained at 298 K. The assignments in Table 5 were unambiguously determined with the aid of two-dimensional techniques such as COSY, HMQC, and HMBC.
[b] The values with this superscript may be interchanged.

**Table 6** $^{13}C$ NMR Chemical Shifts (δ) for 1,2-Dithiete 1,1,2-Trioxides **32**[a]

| C | 32b | 32f | 32g | 32h |
|---|---|---|---|---|
| 1 | 154.7 | 151.4 | 166.6 | 159.5 |
| 2 | 150.6 | 165.3 | 149.8 | 150.9 |
| 3 | 25.7 | 26.9 | 27.7 | 26.8 |
| 4 | 18.6 | 19.8 | 19.4 | 18.5 |
| 5 | 76.5 | 102.9 | 103.4 | 75.5 |
| 6 | 85.4 | 88.3 | 87.0 | 92.7 |
| α | 19.6 | –0.5 | –4.4 | 35.2 |
| β | 13.6 | | 18.4 | 30.8 |
| γ | | | 26.7 | |
| α′ | 12.4 | –0.2 | –4.0 | 27.5 |
| β′ | 13.9 | | 18.4 | 31.1 |
| γ′ | | | 26.7 | |

[a] $^{13}C$ NMR spectra (75 MHz) of samples in $CDCl_3$ with TMS as internal reference were obtained at 298 K. The assignments in Table 6 were unambiguously determined with the aid of two-dimensional techniques such as COSY, HMQC, and HMBC.

$^{13}$C NMR (75 MHz, $CDCl_3$): see Figure 1 and Table 6.

MS (CI, isobutane): *m*/*z* (%) = 303 (19) [$MH^+$], 223 (100) [$MH^+$ – '$SO_2$' – 'O'].

HRMS: *m*/*z* [$MH^+$] calcd for $C_{14}H_{23}O_3S_2$: 303.1089; found: 303.1076.

### Rearrangement of α-Bulky-Substituted Bis(propargyloxy) Disulfides; General Procedure

A $CHCl_3$ soln of the appropriate bis(propargyloxy) disulfide was heated under reflux for the time indicated in Table 4. This reaction was characterized by the soln turning orange-red in color. After cooling of the mixture to r.t., the solvent was evaporated under reduced pressure and the residue was purified by chromatography (silica gel). All products were obtained as yellow liquids.

### (3*E*,6*E*)-3,6-Bis(2,2-dimethylpent-4-enylidene)-2-oxa-5,7-dithiabicyclo[2.2.1]heptane 5-Oxides (34b/35b)

See Table 4. The products were isolated and separated by chromatography (silica gel, *n*-hexane–EtOAc, 200:5→95:5→8:1).

#### Major Isomer 34b

IR (neat): 1002, 1058 (S=O), 1637, 2359, 2960, 3416 $cm^{-1}$.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 6.69 [br s, 1 H (CH−O)], 6.19 [br s, 1 H (=CH of 'SO' side)], 5.73 [br s, 1 H (CH−SO)], 5.80–5.65 (m, 2 H), 5.21 [s, 1 H (=CH of 'O' side)], 5.14–5.01 (m, 4 H), 2.20 (dd, *J* = 7.4, 1.0 Hz, 2 H), 2.12 (dd, *J* = 7.4, 1.0 Hz, 2 H), 1.25 (s, 3 H), 1.24 (s, 3 H), 1.21 (s, 3 H), 1.19 (s, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 150.7 (=C−SO), 145.7 [=CH−$C(CH_3)_2$ of 'SO' side], 141.6 (=C−O), 134.6 ($CH_2$=CH−), 133.7 ($CH_2$=CH−), 119.1 (=$CH_2$), 118.3 (=$CH_2$), 117.6 [=CH−$C(CH_3)_2$ of 'O' side], 82.0 (−CH−O), 69.4 (−CH−SO), 48.7 (−$CH_2$−), 47.6 (−$CH_2$−), 39.0 [−$C(CH_3)_2$], 34.8 [−$C(CH_3)_2$], 29.5 (−$CH_3$), 28.6 (−$CH_3$), 28.4 (−$CH_3$), 27.9 (−$CH_3$).

MS (CI, $CH_4$): *m*/*z* (%) = 338 (16) [$M^+$], 197 (100), 157 (43).

HRMS: *m*/*z* [$M^+$] calcd for $C_{18}H_{26}O_2S_2$: 338.1374; found: 338.1373.

#### Minor Isomer 35b

IR (neat): 1075 (S=O), 1466, 1672, 2253, 2360, 2965 $cm^{-1}$.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 6.51 [br s, 1 H (CH−O)], 5.86 [br s, 1 H (=CH of 'SO' side)], 5.77 [br s, 1 H (CH−SO)], 5.90–5.62 (m, 2 H), 5.51 [s, 1 H (=CH of 'O' side)], 5.14–5.02 (m, 4 H), 2.17 (dm, *J* = 7.4 Hz, 2 H), 2.15 (dm, *J* = 7.4 Hz, 2 H), 1.23 (s, 3 H), 1.20 (s, 6 H), 1.19 (s, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 144.7 (=C−SO), 141.7 (=C−O), 140.6 [=CH−$C(CH_3)_2$ of 'SO' side], 135.0 ($CH_2$=CH−), 133.9 ($CH_2$=CH−), 118.7 [=CH−$C(CH_3)_2$ of 'O' side], 118.6 (=$CH_2$), 117.7 (=$CH_2$), 82.8 (−CH−O), 64.0 (−CH−SO), 48.9 (−$CH_2$−), 47.6 (−$CH_2$−), 38.2 [−$C(CH_3)_2$], 34.8 [−$C(CH_3)_2$], 30.5 (−$CH_3$), 28.7 (−$CH_3$), 28.2 (−$CH_3$), 27.4 (−$CH_3$).

MS (CI, $CH_4$): *m*/*z* (%) = 338 (56) [$M^+$], 201 (52), 197 (100).

HRMS: *m*/*z* [$M^+$] calcd for $C_{18}H_{26}O_2S_2$: 338.1374; found: 338.1358.

### Rearrangement of Bis(α,α-dimethylpropargyloxy) Disulfide 14

A 1.6 M soln of *n*-BuLi in *n*-hexane (11.5 mmol) was added to a stirred soln of the appropriate alcohol (10 mmol) in anhyd $Et_2O$ (100 mL) at –78 °C under $N_2$ atmosphere. After 30 min, a soln of $S_2Cl_2$ (5 mmol) in anhyd $Et_2O$ (50 mL) was added dropwise to the reaction mixture for 30 min. Then the reaction mixture was warmed to 0 °C, the amine hydrochloride salt precipitated as a white solid, and the color of the reaction mixture turned to red-brown. After stirring of the reaction mixture for 20 min at 0 °C, the salt was collected by filtration under vacuum and the $Et_2O$ soln was washed with ice water. Drying ($MgSO_4$) and removing of the solvent under reduced pressure were carried out under external cooling. Immediately after evaporation, the cold solvent required for the next step was added. At the end of the reaction, one isomer was obtained. After a few hours at r.t., it converted into a mixture of two isomers (1.25:1 ratio), in which a new isomer is the major one; total yield: 39%.

### 3,6-Bis(isopropylidene)-2-oxa-5,7-dithiabicyclo[2.2.1]heptane 5-Oxides (36/37)

The products were isolated and separated by chromatography (silica gel, *n*-hexane–EtOAc, 5:1→2:1).

#### Minor Isomer 36

Compound **36** was the minor isomer in the equilibrium after sulfoxide inversion (more polar); this is the actual product in this reaction.

IR (neat): 1046 (S=O), 1444, 1654, 1701, 2978 $cm^{-1}$.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 6.48 [d, *J* = 0.9 Hz, 1 H (CH–O)], 5.64 [br d, *J* = 0.9 Hz, 1 H (CH–SO)], 2.19 (s, 3 H), 2.03 (s, 3 H), 1.84 (br s, 3 H), 1.66 (br s, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 146.1 (=C–), 143.4 (=C–), 137.1 (=C–), 111.4 (–C=C–O), 85.4 (–CH–O), 71.0 (–CH–SO), 23.8 (–$CH_3$), 22.2 (–$CH_3$), 20.2 (–$CH_3$), 17.7 (–$CH_3$).

MS (CI, $CH_4$): *m*/*z* (%) = 231 (71) [$MH^+$], 230 (63) [$M^+$].

HRMS: *m*/*z* [$MH^+$] calcd for $C_{10}H_{15}O_2S_2$: 231.0513; found: 231.0506.

#### Major Isomer 37

Compound **37** was the major isomer in the equilibrium after sulfoxide inversion (less polar).

IR (neat): 1053 (S=O), 1446, 1654, 1701, 2919 $cm^{-1}$.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 6.38 [br d, *J* = 0.6 Hz, 1 H (CH–O)], 5.64 [br d, *J* = 0.6 Hz, 1 H (CH–SO)], 2.02 (s, 3 H), 1.96 (s, 3 H), 1.82 (s, 6 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 139.6 (=C–), 137.8 (=C–), 137.6 (=C–), 112.5 (–C=C–O), 86.5 (–CH–O), 64.8 (–CH–SO), 21.8 (–$CH_3$), 20.7 (–$CH_3$), 20.0 (–$CH_3$), 17.8 (–$CH_3$).

MS (CI, $CH_4$): *m*/*z* (%) = 230 (69) [$M^+$].

HRMS: *m*/*z* [$M^+$] calcd for $C_{10}H_{14}O_2S_2$: 230.0435; found: 230.0445.

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis. It includes experimental details and characterization data for all synthesized compounds.

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