Synthetic potentialities of sulfonylsulfonium salts: a new approach to the preparation of disulfonium dications

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A new efficient method for the generation of disulfonium dications whose subsequent hydrolysis selectively affords monosulfoxides was developed based on the oxidation of bis-sulfides by trifluoromethanesulfonic anhydride.

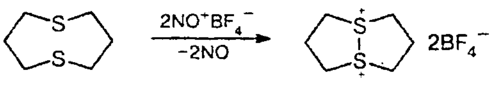
Key words: trifluoromethanesulfonic anhydride, selective oxidation of bis-sulfides, disulfonium dications, monosulfoxides of bis-sulfides.

Compounds whose molecules contain two adjacent positively charged heteroatoms are unusual and rare. In structures of this type, unlike dications with spatially separated centers and monocations, the mutual influence of two positively charged reaction centers is a maximum, which can result in the appearance of new unusual properties. The study of these compounds is of considerable theoretical interest and attracts attention of many researchers. Various 1,2-dications containing adjacent onium atoms of phosphorus,[1] nitrogen,[2] sulfur,[3] selenium,[4] and tellurium[5] and dications with two different heteroatoms[6] have been synthesized during recent years.

Disulfonium dications represent the most studied type of dications. The first unsuccessful attempts of their synthesis go back to the beginning of the century in a study of the possibility to alkylate both sulfur atoms in disulfides.[7] Therefore, for a long time S—S dications were considered only as labile intermediates in some reactions.

The first bicyclic S—S dication stable at room temperature has been prepared[8] by the oxidation of bis-sulfide using the salt of the nitrosyl cation (Scheme 1).

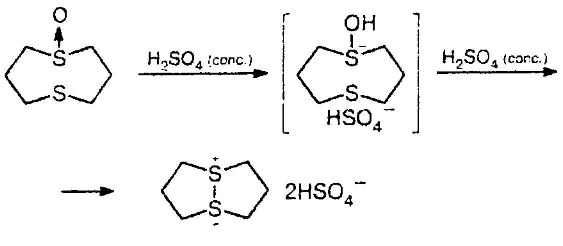
Scheme 1



The use of this method is restricted by side nitrosation processes and the complex apparatus required.

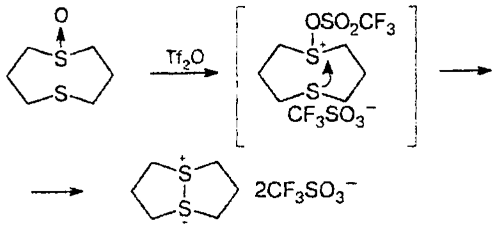
Yet another approach to the formation of the disulfonium-dication function is also based on the creation of a bond between the sulfur atoms in intramolecular nucleophilic substitution in the hydroxysulfonium salt generated from a sulfoxide[9] (Scheme 2).

Scheme 2



At present, the treatment of monosulfoxides of bis-sulfides[10] with trifluoromethanesulfonic anhydride (Tf_2O) is the most versatile method of the preparation of S—S dications (Scheme 3).

Scheme 3



The necessity of the pre-oxidation of the starting bis-sulfides to monosulfoxides is an evident disadvantage of these methods. It is known[11] that the oxidation of sulfides to sulfoxides is often accompanied by their overoxidation to sulfones, and the problem of the selective preparation of monoxides from bis-sulfides remains yet poorly studied.

Thus, analysis of the published data shows that, despite a great interest in studying S—S dications, the

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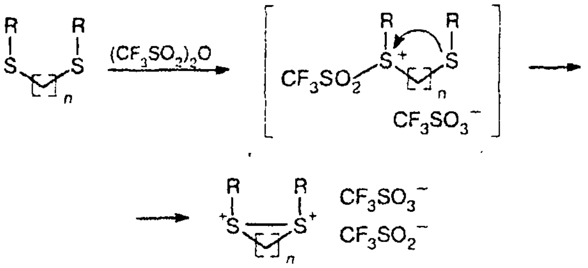
development of simple and convenient methods for their generation is an urgent problem.

In a continuation of our studies of the reactions of trifluoromethanesulfonic anhydride with sulfides, we studied its reactions with bis-sulfides. We have previously shown[12] that the treatment of dimethyl sulfide with Tf_2O affords a new complex, which represents a sulfonylsulfonium salt. The latter contains a good leaving trifluoromethylsulfonyl group and is a sufficiently reactive sulfonium electrophile.[13]

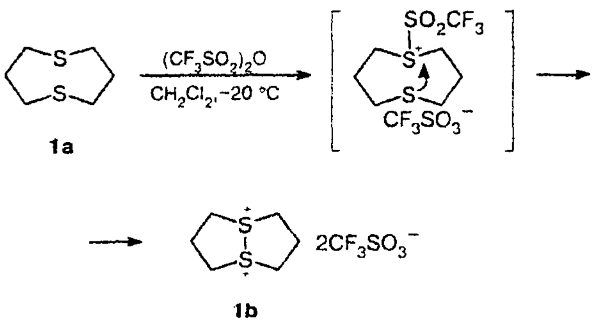
We assumed that the treatment of bis-sulfides with the appropriate structure with Tf_2O can result in the intramolecular nucleophilic substitution of the trifluoromethylsulfonyl group of an intermediate sulfonylsulfonium salt by the second sulfur atom, which would give disulfonium dications (Scheme 4).

Scheme 4



To check this possibility, we first studied the reaction of Tf_2O with 1,5-dithiocane (**1a**). In this case, the dication that would be formed should possess, according to the published data,[14] a stability sufficient for its isolation in individual form. Indeed, the addition of 1,5-dithiocane to a solution of Tf_2O (1.2 equiv.) in CH_2Cl_2 cooled to −20 °C results in an exothermic reaction and is accompanied by yellow coloration of the reaction mixture. The solution is gradually discolored in 1 h, and a white precipitate is formed. The ^1H NMR spectrum of the isolated salt coincides with that of previously[15] synthesized 1,5-dithioniabicyclo[3.3.0]octane (Scheme 5).

Scheme 5



Analysis of the ^{19}F NMR spectrum of the isolated disulfonium dication gave an unexpected result. According to the reaction equation of the oxidation of bis-sulfide **1a** with trifluoromethanesulfonic anhydride, trifluoromethanesulfinate and trifluoromethanesulfonate anions should be counterions of the S—S dication that formed.

However, according to the data from ^{19}F NMR spectroscopy, only a signal at δ −78, which corresponds to trifluoromethanesulfonate anion as the counterion of S—S dication **1b**, was observed. We did not observe signals in the region of δ −90, where trifluoromethanesulfinate anions should resonate.[16]

Probably, this can be explained by the anion exchange between the trifluoromethanesulfinate anion primarily formed in the redox reaction and the unconsumed trifluoromethanesulfonic anhydride, which affords a mixed anhydride and sulfonate anion (Scheme 6).

Scheme 6

$$CF_3SO_2^- + (CF_3SO_2)_2O \rightarrow$$

$$\rightarrow CF_3S(O)OSO_2CF_3 + CF_3SO_3^-$$

It has previously[17] been shown that the treatment of a suspension of potassium trifluoromethanesulfinate in CH_2Cl_2 with trifluoromethanesulfonic anhydride affords potassium trifluoromethanesulfonate.

This reaction scheme assumes the necessity of using 2 equiv. of Tf_2O per mole of bis-sulfide. However, the optimum ratio of bis-sulfide to trifluoromethanesulfonic anhydride is 1 : 1.2, and dication **1b** was isolated in a yield of 84%. Moreover, we showed by additional experiments that the use of larger amounts of the anhydride does not result in an increase in the yield of the dication. Similar discrepancy of the stoichiometry with the assumed reaction equation has previously been noted[17] for the oxidation of trithiocarbonates with trifluoromethanesulfonic anhydride.

The data obtained could be explained by the fact that other reactants along with Tf_2O participated in the reaction as oxidants. Our primary assumption that dioxygen dissolved in Tf_2O and in the solvent served as the oxidant was not confirmed by a control experiment on the oxidation in degassed solvent and inert atmosphere.

We believe that the general reaction scheme is more complex and includes subsequent reduction or disproportionation of mixed trifluoromethanesulfonic-trifluoromethanesulfinic anhydride, resulting in products of deeper oxidation. Then the amount of trifluoromethanesulfonic anhydride necessary for the oxidation of bis-sulfide to the disulfonium dication can be smaller than 2 equiv., which is assumed by the anion exchange scheme. This is indirectly confirmed by spectral data obtained by the study of the reaction directly in an NMR tube (Fig. 1). The ^{19}F NMR spectrum of a mixture obtained by mixing bis-sulfide **1a** with Tf_2O at −70 °C contains, along with signals at δ −79 to −78 corresponding to the starting anhydride and triflate anion, a weak signal of the trifluoromethanesulfinate anion at δ −88 and a signal at δ −45 ppm, which probably corresponds to the CF_3S fragment bound to the electron-withdrawing group. The exposure of the reaction mixture to room temperature for 15 min results in the disappearance of the signal of the trifluoromethanesulfinate anion. Immediately after the mixing of the reactants, the ^{19}F NMR spectrum exhibits a signal at δ −71, which also disappears when the reaction is over. The lack of published data does not allow us to propose its reliable assignment and to determine a specific structure corresponding to the signal at δ −45. However, these facts also indicate that the reaction that takes place is more complex. Subsequent studies using special methods are apparently required for reliable determination of the mechanism of the reduction of Tf_2O by bis-sulfides and the overall reaction equation.

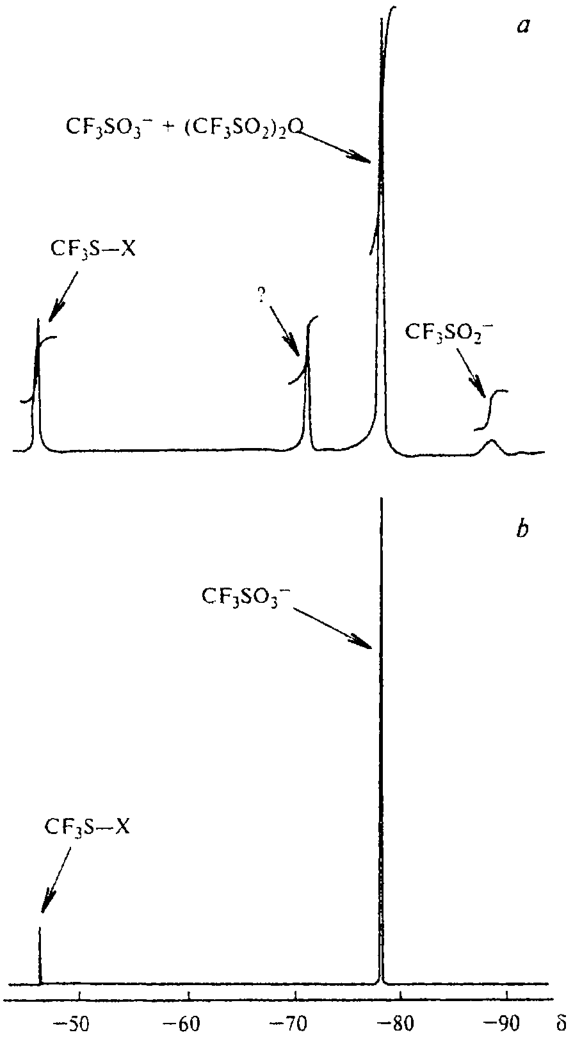
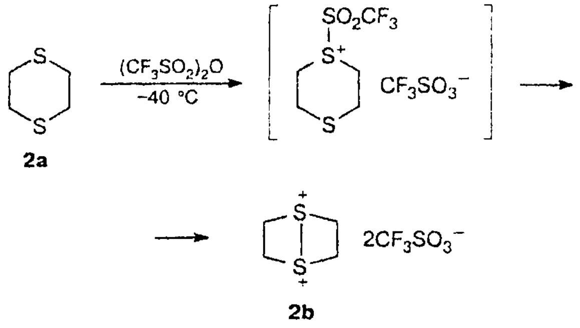


Fig. 1. ^{19}F NMR (CD_3CN) spectra of the reaction mixture of 1,5-dithiocane and Tf_2O cooled to −70 °C (*a*) and exposed to 20 °C for 15 min (*b*).

With the purpose of revealing the potentialities of the proposed method, we oxidized 1,4-dithiane with trifluoromethanesulfonic anhydride. The formation of the S—S dication, a 1,4-dithiane derivative, is the most difficult[10] as compared to other cyclic and acyclic dications described to date. This is related to a substantial angular strain that appears when two four-membered rings are formed. As for the oxidation of sulfide **1a**, the reaction of dithiane **2a** with trifluoromethanesulfonic anhydride does not stop at the step of sulfonylsulfonium salt formation, but results in the strained disulfonium dication (**2b**) (Scheme 7). Its formation was confirmed by the spectral data (^1H NMR).

Scheme 7



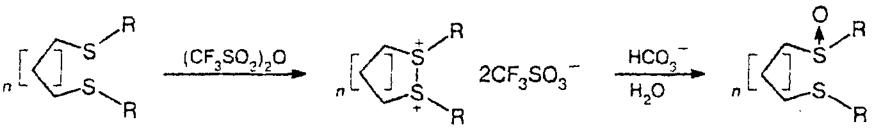
We also oxidized a wider range of substrates. Since the major part of disulfonium dications are very labile compounds, which can barely be isolated in individual form, if at all, they were characterized by the hydrolysis products, *viz*., the corresponding sulfoxides (Table 1). Hydrolysis of disulfonium dications to monosulfoxides is the most widely used proof for their formation because it affords easily identifiable compounds and occurs in quantitative yield without the formation of by-products[18] (Scheme 8).

Generalizing the obtained experimental data, note that the stability of the generated S—S dications strongly

Table 1. Oxidation products of bis-sulfides by trifluoromethanesulfonic anhydride followed by hydrolysis

Sulfide	Oxidation conditions		Product	Yield
	T/°C	*t*/h		(%)
1a	−20—0	1	**1c**	71
2a	−40—−20	12	**2c**	31
3a	−40—−20	12	**3c**	55
4a	−70—−60	4	**4c**	63
5a	−70—−60	3	**5c**	44
6a	−40—−20	2	**6c**	72
7a	−40—−20	2	**7c**	85

Scheme 8



1a—7a $n = 0, 1, 2$ **1c—7c**

$n = 1$, R + R = $-(CH_2)_3-$ (**1**); $n = 0$, R + R = $-(CH_2)_2-$ (**2**);
$n = 1$, R + R = $-(CH_2)_2-$ (**3**); $n = 1$, R + R = o-$CH_2C_6H_4CH_2-$ (**4**);
$n = 0$, R = CH_3 (**5**); $n = 1$, R = CH_3 (**6**); $n = 2$, R = CH_3 (**7**)

depends on angular strains appearing in new rings when an additional S—S bond is formed. Five- and six-membered rings are closed most easily, and the closure of strained four-membered rings is much more difficult. For example, on going from eight-membered sulfide **1a**, whose dication contains two five-membered rings, to dication **2a**, that forms the disulfonium dication with two four-membered rings, we observed a decrease in the yield of the corresponding sulfoxides from 70 to 30%.

The formation of disulfonium dications from acyclic bis-sulfides **5a—7a** also obeys the regularity mentioned. The yields of the corresponding monosulfoxides increase on going from compounds containing two methylene fragments between the sulfur atoms to those containing three and then four fragments (see Table 1). The oxidation of bis-sulfide **5a** to form the target S—S dication is possible only at temperatures below −60 °C. At higher temperatures, we observed the formation of a mixture of unidentified sulfonium salts, which is most likely related to transmethylation between the disulfonium dication formed and the starting bis-sulfide. Similar reactions with methyl group transfer are characteristic of the strained S—S dications.[19]

Disulfonium dications containing benzyl substituents at the sulfur atom are most labile. For example, the reaction of sulfide **4a** with trifluoromethanesulfonic anhydride at moderate temperatures is complicated by side reactions leading to a mixture of sulfonium salts which are difficult to identify and whose formation can be reduced to a minimum when the reaction is performed with strong cooling. The oxidation of 1,3,4,6-tetrahydrobenzo-2,5-dithiocine that should give the disulfonium dication with strained four-membered rings could not be performed even at very low temperatures (Scheme 9).

This is probably related to an elevated mobility of the benzyl group and instability of intermediate sulfonylsulfonium salts. It has previously been shown[12] that the treatment of benzyl methyl sulfide with trifluoromethanesulfonic anhydride even at −40 °C affords not the sulfonylsulfonium salt, but dibenzyl(methyl)sulfonium triflate.

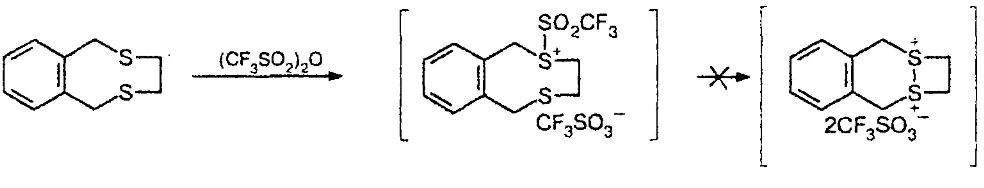
Thus, we developed a new method of the synthesis of disulfonium dications based on the oxidation of cyclic and acyclic bis-sulfides by trifluoromethanesulfonic anhydride and demonstrated its potentialities and limitations. The role of trifluoromethanesulfonic anhydride as an oxidant in these transformations was studied. Based on the hydrolysis of intermediate disulfonium dications, we developed a new selective method of the oxidation of bis-sulfides to monosulfoxides without the side formation of oxidation products of both sulfur atoms.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AC-200P (200 and 50 MHz, respectively) and Varian VXR-400 (400 and 100 MHz, respectively) spectrometers in $CDCl_3$, CD_3CN, and $(CD_3)_2CO$ using Me_4Si as the internal standard. ^{19}F NMR spectra were obtained on a Bruker AC-200P instrument (200 MHz) using CD_3CN as the solvent and CCl_3F as the internal standard. Solvents were dehydrated according to standard procedures. Trifluoromethanesulfonic anhydride was prepared from the corresponding acid by the previously described method.[20]

Synthesis of cyclic bis-sulfides (general procedure). A mixture of the corresponding alkanedithiol (20 mmol) and dibromoalkane (20 mmol) in anhydrous EtOH (50 mL) was added dropwise for 1.5 h with stirring to a solution (heated to boiling) of sodium ethoxide (from 1 g of sodium) in anhydrous EtOH (200 mL). The reaction mixture was boiled for 1 h, and then the major portion of the solvent was distilled off. The residue was treated with water (150 mL) and extracted with chloroform (4×40 mL), the extract was dried with $CaCl_2$, and the reaction product was additionally purified.

Scheme 9



1,5-Dithiocane (1a) was synthesized from propanedithiol and 1,3-dibromopropane. The reaction product was extracted with hot hexane, the solvent was evaporated, and the residue was distilled *in vacuo*. Compound **1a** was isolated in 41% yield (1.2 g), b.p. 81—84 °C (0.8 Torr) (*cf.* Ref. 21: b.p. 245—246 °C). ^{1}H NMR ($CDCl_3$), δ: 2.58—2.04 (m, CH_2S); 1.92—1.78 (m, $CH_2C\underline{H}_2CH_2$); intensity ratio 2 : 1.

1,4-Dithiane (2a) was synthesized from ethanedithiol and 1,2-dibromoethane. The reaction product was recrystallized from hexane; the yield of compound **2a** was 1.5 g (64%), m.p. 112—113 °C (*cf.* Ref. 22: m.p. 112—113 °C).

1,4-Dithiepane (3a) was synthesized from ethanedithiol and 1,3-dibromopropane. The reaction product was extracted with hot hexane, the solvent was evaporated *in vacuo*, and the residue was purified by column chromatography using hexane as the eluent. The yield of compound **3a** was 1.6 g (61%), m.p. 48—49 °C (*cf.* Ref. 21: m.p. 47 °C).

1,4,5,7-Tetrahydro-3*H*-benzo-2,6-dithionine (4a) was synthesized from propane-1,3-dithiol and 1,2-bis(bromomethyl)benzene. The reaction product was purified by column chromatography using a hexane—diethyl ether (10 : 1) mixture as the eluent. The yield of compound **4a** was 2.4 g (61%), m.p. 83—84 °C (*cf.* Ref. 23: m.p. 85 C). ^{1}H NMR ($CDCl_3$), δ: 7.29—7.22 (m, H arom.); 3.76 (s, $ArCH_2S$); 2.56 (t, CH_2S, J = 5.7 Hz); 1.87—1.78 (m, CH_2); intensity ratio 2 : 2 : 2 : 1.

Preparation of acyclic bis-sulfides (general procedure). Powdered KOH (22.0 g, 0.4 mol) was added with stirring to a solution of methylisothiouronium sulfate (27.8 g, 0.1 mol) in methanol (100 mL). After 15 min, the corresponding dibromoalkane (0.04 mol) was added dropwise to the reaction mixture. After boiling for 2 h, the reaction mixture was treated with cold water (300 mL), the aqueous phase was extracted with chloroform, the extract was dried with $MgSO_4$, the solvent was evaporated, and the residue was distilled *in vacuo*.

Methyl 2-(methylsulfanyl)ethyl sulfide (5a) was synthesized from 1,2-dibromoethane in 80% yield (3.9 g), b.p. 180—182 °C (*cf.* Ref. 24: b.p. 181 °C). ^{1}H NMR ($CDCl_3$), δ: 2.68 (s, CH_2S); 2.09 (s, CH_3S); intensity ratio 2 : 3.

Methyl 3-(methylsulfanyl)propyl sulfide (6a) was synthesized from 1,3-dibromopropane in 52% yield (2.8 g), b.p. 86—88 °C (12 Torr) (*cf.* Ref. 23: b.p. 86—87 °C (12 Torr)). ^{1}H NMR ($CDCl_3$), δ: 2.60 (t, CH_2S, J = 7.2 Hz); 2.11 (s, CH_3S); 1.89 (quint, CH_2, J = 7.2 Hz); intensity ratio 2 : 3 : 1.

Methyl 4-(methylsulfanyl)butyl sulfide (7a) was synthesized from 1,4-dibromobutane in 86% yield (5.2 g), b.p. 115—117 °C (25 Torr) (*cf.* Ref. 25: b.p. 115 C (26 Torr)). ^{1}H NMR ($CDCl_3$), δ: 2.54—2.48 (m, CH_2S); 2.09 (s, CH_3S); 1.73—1.67 (m, $CH_2C\underline{H}_2C\underline{H}_2CH_2$); intensity ratio 2 : 3 : 2.

1,5-Dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (1b). A solution of 1,5-dithiocane (0.89 g, 6 mmol) in anhydrous dichloromethane (10 mL) was added dropwise with stirring to a solution of trifluoromethanesulfonic anhydride (1.1 mL, 6.5 mmol) in anhydrous CH_2Cl_2 (50 mL) cooled to −20 °C. The reaction mixture was left for 1 h at −20 °C. The product was filtered off, washed with anhydrous CH_2Cl_2, and dried *in vacuo*. The yield of compound **1b** was 2.0 g (78%), m.p. 130—131 °C (with decomp.). ^{1}H NMR (CD_3CN), δ: 3.75—2.80 (m, $CH_2—S^+$); 2.60—2.20 (m, CH_2); intensity ratio 2 : 1. ^{19}F NMR (CD_3CN), δ: −78.60 (CF_3).

Synthesis of monosulfoxides of bis-sulfides (general procedure). A solution of the corresponding bis-sulfide (5 mmol) in anhydrous CH_2Cl_2 (20 mL) was added dropwise to a solution of trifluoromethanesulfonic anhydride (1 mL, 6 mmol) in anhydrous CH_2Cl_2 (50 mL) cooled to −70 °C. After stirring for several h (TLC monitoring, see Table 1), the reaction mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (20 mL). The organic phase was separated, and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined extracts were dried with $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography using a chloroform—methanol (9 : 1) mixture.

1,5-Dithiocane 1-oxide (1c), yield 71%, oil. ^{1}H NMR ($(CD_3)_2CO$), δ: 3.20—3.02 (m, $CH_2S=O$); 2.64 (t, CH_2S, J = 6.0 Hz); 2.38—2.06 (m, CH_2); intensity ratio 1 : 1 : 1. The ^{13}C NMR spectrum is identical with that described previously.[26]

1,4-Dithiane 1-oxide (2c), yield 31%, m.p. 125—126 °C (*cf.* Ref. 26: m.p. 119—122 °C). ^{1}H NMR ($(CD_3)_2CO$), δ: 3.67—3.52 (m, H_{ax}, CH_2S); 3.20—2.93 (m, $CH_2S=O$); 2.62—2.48 (m, $H_{eq}CH_2S$); intensity ratio 1 : 2 : 1. ^{13}C NMR ($(CD_3)_2CO$), δ: 46.68 (C(2), C(6)); 18.59 (C(3), C(5)).

1,4-Dithiepane 1-oxide (3c), yield 55%, oil. The ^{1}H NMR spectrum is identical with that described previously.[26] ^{13}C NMR ($(CD_3)_2CO$), δ: 55.32 (C(1)); 47.61 (C(7)); 30.53 (C(3)); 24.20 (C(5)); 20.85 (C(6)).

1,4,5,7-Tetrahydro-3*H*-benzo-2,6-dithionine 2-oxide (4c), yield 63%, m.p. 185—186 °C. Found (%): C, 57.89; H, 6.20. $C_{11}H_{14}OS_2$. Calculated (%): C, 58.37; H, 6.23. ^{1}H NMR (CD_3CN). δ: 7.60—7.47 (m, H arom.); 4.46—4.31 (m, $ArCH_2S=O$); 4.12—3.96 (m, CH_2S); 3.10—2.87 (m, CH_2S, $CH_2S=O$); 2.64—2.00 (m, CH_2); intensity ratio 2 : 1 : 1 : 2 : 1. ^{13}C NMR (CD_3CN), δ: 141.68 (C(11a)); 131.99, 131.65, 129.70, 127.96 (C(8), C(9), C(10), C(11)); 129.05 (C(7a)); 55.38 (C(1)); 44.88 (C(3)); 35.88 (C(7)); 35.47 (C(5)); 23.23 (C(4)).

Methyl 2-(methylsulfanyl)ethyl sulfoxide (5c), yield 44%, oil. ^{1}H NMR (CD_3CN), δ: 3.08—2.72 (m, CH_2S, $CH_2S=O$); 2.62 (s, $CH_3S=O$); 2.12 (s, CH_3S); intensity ratio 4 : 3 : 3. The ^{13}C NMR spectrum is identical with that described previously.[26]

Methyl 3-(methylsulfanyl)propyl sulfoxide (6c), yield 72%, oil. ^{1}H NMR (CD_3CN), δ: 2.88—2.80 (m, $CH_2S=O$); 2.68 (t, CH_2S, J = 6.9 Hz); 2.61 (s, $CH_3S=O$); 2.12 (s, CH_3S); 2.10—2.05 (m, CH_2); intensity ratio 2 : 2 : 3 : 3 : 2. The ^{13}C NMR spectrum is identical with that described previously.[26]

Methyl 4-(methylsulfanyl)butyl sulfoxide (7c), yield 85%, oil. ^{1}H NMR (CD_3CN), δ: 2.58—2.52 (m, $CH_2S=O$); 2.40 (s, $CH_3S=O$); 2.36 (t, CH_2S, J = 7.1 Hz); 1.91 (s, CH_3S); 1.72—1.66 (m, $SCH_2CH_2C\underline{H}_2CH_2S=O$); 1.62—1.55 (m, $SCH_2C\underline{H}_2CH_2CH_2S=O$); intensity ratio 2 : 3 : 2 : 3 : 2 : 2. The ^{13}C NMR spectrum is identical with that described previously.[26]

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References

1. R. W. Alder, C. Ganter, M. Gil, R. Glieter, C. J. Harris, S. E. Harris, H. Lange, A. G. Orpen, and P. N. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1643.
2. R. W. Alder and R. B. Session, *J. Am. Chem. Soc.*, 1979, **101**, 3651.
3. W. K. Musker, *Acc. Chem. Res.*, 1980, **13**, 200.
4. H. Fujihara, A. Nakamura, R. Akaishi, and N. Furukawa, *Chem. Lett.*, 1990, 393.
5. H. Fujihara, T. Ninoi, R. Akaishi, T. Erata, and N. Furukawa, *Tetrahedron Lett.*, 1991, **32**, 4537.
6. H. Fujihara, H. Mima, J.-J. Chiu, and N. Furukawa, *Tetrahedron Lett.*, 1990, **31**, 2307.
7. G. Hesse and R. Thieme, *Lieb. Ann. Chem.*, 1965, **686**, 64.

8. W. K. Musker and P. B. Rouch, *J. Am. Chem. Soc.*, 1976, **98**, 6745.
9. H. Fujihara, A. Kawada, and N. Furukawa, *Heterocycles*, 1986, **24**, 17.
10. H. Fujihara, R. Akaishi, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, 1987, 931.
11. W. K. Musker, T. L. Wolford, and P. B. Rouch, *J. Am. Chem. Soc.*, 1978, **100**, 6416.
12. V. G. Nenajdenko, P. V. Vertelezkij, A. B. Koldobskij, I. V. Alabugin, and E. S. Balenkova, *J. Org. Chem.*, 1997, **62**, 2483.
13. N. E. Shevchenko, A. S. Karpov, E. P. Zakurdaev, V. G. Nenaidenko, and E. S. Balenkova, *Khim. Geterotsikl. Soedin.*, 2000, 171 [*Chem. Heterocycl. Compd.*, 2000 (Engl. Transl.)].
14. F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2563.
15. N. Furukawa, A. Kawada, and T. Kawai, *J. Chem. Soc., Chem. Commun.*, 1984, 1151.
16. J. B. Hendrickson, D. A. Judelson, and T. Chancellor, *Synthesis*, 1984, 320.
17. G. Maas and P. J. Stang, *J. Org. Chem.*, 1981, **46**, 1606.
18. W. K. Musker, T. L. Wolford, and P. B. Rouch, *J. Am. Chem. Soc.*, 1978, **100**, 6416.
19. H. Naka, T. Maruyama, S. Sato, and N. Furukawa, *Tetrahedron Lett.*, 1999, **40**, 345.
20. P. J. Stang, M. Hanack, and L. R. Subramanian, *Synthesis*, 1982, 85.
21. N. B. Tucker and E. E. Reid, *J. Am. Chem. Soc.*, 1933, **55**, 775.
22. *Organic Synthesis*, Ed. N. Rabjohn, Wiley, New York, 1963, **4**, 1026 pp.
23. D. W. Allen, P. N. Brauton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc., C*, 1971, 3454.
24. D. M. Sweeny, S. I. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, 1955, **77**, 6521.
25. D. Jerchel, L. Pippelholfer, and D. Renner, *Chem. Ber.*, 1954, **87**, 947.
26. P. B. Rouch and W. K. Musker, *J. Org. Chem.*, 1978, **43**, 4295.

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