DOI: 10.1002/ejoc.200600151

# Generation and Rearrangements of Thioacetaldehyde *S*-Sulfide (Methylthiosulfine) and Thioacetone *S*-Sulfide (Dimethylthiosulfine)

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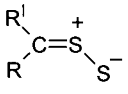
**Keywords:** Matrix isolation / Density functional calculations / Photoisomerizations / Reaction mechanisms / Sulfur compounds

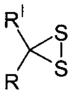
Matrix isolation spectroscopy allows the direct identification of ylides **1b** and **1c**. They are generated by flash vacuum pyrolysis of the 1,2,4-trithiolanes **3b** and **3c**. Photochemical activation of the thiosulfines **1b** and **1c** initiates ring closure to the corresponding dithiiranes **2b** and **3b**. The presence of a methyl group in thiosulfines **1b** and **1c** opens a new reaction channel for their thermal transformation, namely a [1,4]-H shift with formation of vinyldisulfanes **5**. The results of the matrix studies are supported by preparative runs, in which the products of the pyrolyses were trapped at higher temperatures and their spectra measured in solution under standard conditions.

## Introduction

Recently, remarkable progress was made in the exploration of the labile system thiosulfine (thiocarbonyl *S*-sulfide) **1**/dithiirane **2**.[1]



**1**

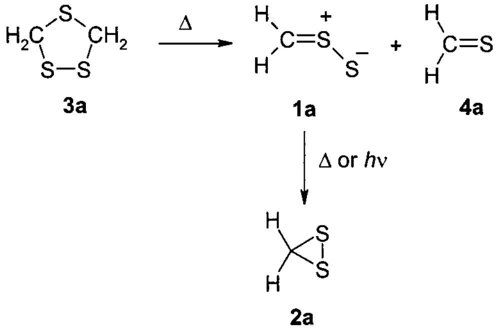


**2**

a: R = H; $R^I$ = H
b: R = H; $R^I$ = $CH_3$
c: R = $CH_3$; $R^I$ = $CH_3$

On the one hand, Ishii and Nakayama elaborated an efficient procedure for the preparation of stable dithiiranes.[2] On the other hand, we described the generation and properties of the parent species **1a** and **2a** (R = R′ = H) taking advantage of matrix isolation techniques and using trithiolane **3a** as the precursor molecule.[3]

In this context it should be recalled that sterically crowded dithiiranes are rather unreactive and show no tendency for ring opening with formation of a thiosulfine or for migration of a substituent leading to an ester of the corresponding dithiocarboxylic acid. Such reactions were only discussed in earlier reports for some less hindered candidates.[1] Whereas nucleophilic reagents like secondary amines decompose dithiiranes,[4] platinum(0) reagents smoothly transform dithiirane 1-oxides into stable dithiolato complexes via cleavage of the S–S bond.[5]



What is known about the properties of thiosulfines? In contrast to sulfines $R_2C{=}S{=}O$,[6] which in many instances are stable compounds, there are no reports on the chemical behavior of an isolated thiosulfine. One expects a variety of products, for instance 1,2,4-trithiolanes, 1,2,4,5-tetrathianes, 1,2,3,5,6-pentathiepanes or even 1,2,3,4,5,6-hexathiocanes, resulting from oligomerizations or cycloadditons with thiocarbonyl compounds, which normally are also formed in the standard procedure for generating thiosulfines.[1,2,7] Namely, the method of choice is the cycloreversion of the corresponding 1,2,4-trithiolanes. But other methods, including sulfur transfer to the C=S bond or an "unzipping" of acetylated disulfides are also known.[1]

Aryl-substituted thiosulfines **1** (R = $C_6H_5$, 4-$ClC_6H_4$ or 4-$MeOC_6H_4$) were studied by Huisgen and Rapp and they were shown to behave as typical 1,3-dipoles giving [3+2]-cycloadducts with suitable C=C and C≡C dipolarophiles.[8]

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Thus, thiosulfines belong to the class of "sulfur-centred" 1,3-dipoles and are expected to display similar reactivity as thiocarbonyl *S*-ylides[9] or thiocarbonyl *S*-imides.[10]

The aim of the present study was to matrix-isolate the hitherto unknown methyl-substituted thiosulfines **1b** and **1c**. It was of special interest, whether in these compounds the 1,3-electrocyclic ring closure will compete with a [1,4]-H shift leading to vinyldisulfides. Until now this type of reaction has never been observed in a thiosulfine/dithiirane pair. However, a similar [1,4]-H shift from an alkyl substituent at the negative end of the 1,3-dipole to the thiocarbonyl carbon is known in alkyl-substituted thiocarbonyl *S*-ylides[11] and thiocarbonyl *S*-imides.[12]

## Results and Discussion

### Matrix Studies and Calculations

#### *Dimethylthiosulfine*

Analogously to the earlier described procedure applied to parent 1,2,4-trithiolane (**3a**),[3] its 2,5-dimethyl- and 2,2,5,5-tetramethyl derivatives **3b** and **3c** were pyrolyzed in order to generate thioacetaldehyde *S*-sulfide (methylthiosulfine, **1b**) and thioacetone *S*-sulfide (dimethylthiosulfine, **1c**), respectively. In both cases thermolysis was performed under high vacuum conditions in the gas phase by passing the vapor of the respective precursor through an empty quartz tube (inner diameter 8 mm, length of the heated zone 50 mm), which was directly connected to the cryostat. Immediately after leaving the pyrolysis tube the mixture of products together with a high excess of argon was condensed at a CsI window at 10 K. Typical experiments with **3c** were carried out at temperatures between 500–700 °C. The matrix-isolated products were analyzed by FT-IR and UV/Vis spectroscopy (see Figures 1, 2 and 3).

The most intensive IR absorption at 1274.5 cm$^{-1}$ (C=S stretching vibration) together with a set of characteristic additional bands is attributed to thioacetone (**4c**), as could be shown by comparison with the spectrum of an original sample of thioacetone prepared by flash vacuum pyrolysis of allyl isopropyl sulfide.[13] Two less intense absorptions at 696.0 and 616.8 cm$^{-1}$ belong to **1c**. The unsubstituted sulfine **1a** has its band for the S–S stretching vibration at 622.8 cm$^{-1}$.[3] In addition to the absorptions of **1c** and **4c** there are some additional bands which we ascribe to the mixture of *s-cis*- and *s-trans*-(propen-2-yl)disulfane **5c**. This product, isomeric with **1c**, is formed in the gas phase via a [1,4]-H shift. The ratio of **5c**/**1c** increases when the gas phase thermolysis is performed at higher temperature. That means, the disulfane **5c** is a secondary product formed from the initially generated **1c**. As can be derived from the comparison of the respective IR bands the ratio **5**/**1c** is doubled when the temperature increased from 500 °C to 700 °C. The assignment of the IR-bands attributed to **5c** is based on the comparison with the values calculated for both rotamers (Figure 1). As will be discussed below, the presence of **5c** in the reaction mixture is additionally revealed by the $^{1}$H NMR and $^{13}$C NMR spectra taken at low temperatures.

The presence of small amounts of dimethyldithiirane (**2c**) in the isolated product was evidenced by tiny bands which increased in intensity after irradiation with 366-nm light for a few minutes. This result shows that the photoisomerization of **1c** leads to the dithiirane **2c**. Figure 2 shows the difference FT-IR spectrum taken before and after irradiation compared with calculated absorptions (B3LYP/6-311+G**) of **1c** and **2c**.

The UV spectrum of the reaction mixture shows a strong absorption band at $\lambda_{max}$ = 374 nm, which we attribute to **1c**. This absorption disappears completely upon irradiation with 366 nm-light. The observed band corresponds the intense π → π* transition and is in good agreement with the absorption maximum of the parent thiosulfine **1a** at $\lambda_{max}$ = 356 nm.[3] The values calculated for **1a**, **1b** and **1c** with time dependent density functional theory (TD-DFT) are presented in Table 1 and compared with the experimental data.

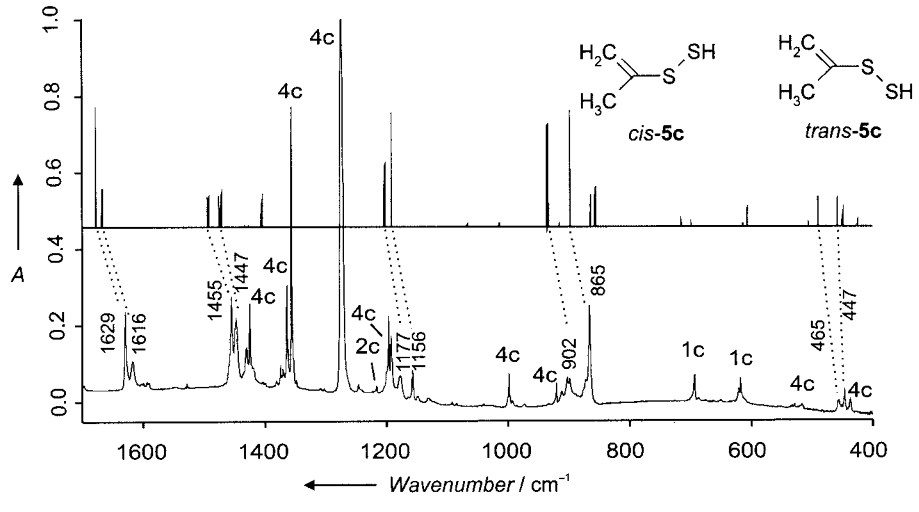


Figure 1. IR spectrum of the matrix-isolated (Ar, 10 K) pyrolysis products (600 °C) of tetramethyltrithiolane (**3c**). Top: computed (B3LYP/6-311+G**) spectra of a 1:1 mixture of *cis*- and *trans*-**5c**.

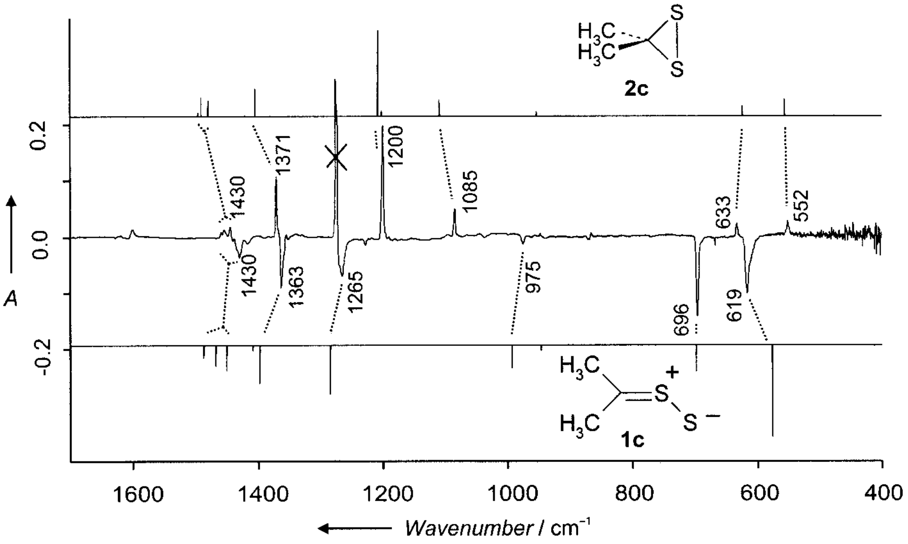


Figure 2. Middle: difference IR spectrum (B–A) monitoring the photo-rearrangement of thiosulfin **1c** (negative bands) into dimethyldithiirane (**2c**) (positive bands). Spectrum A: argon matrix of the pyrolysis products of tetramethyltrithiolane (**3c**), not irradiated; spectrum B: recorded after subsequent irradiation (4 min, $\lambda$ = 366 nm). Top: computed (B3LYP/6-311+G**) IR spectrum of dimethyldithiirane (**2c**). Bottom: computed (B3LYP/6-311+G**) IR spectrum of dimethyl thiosulfine (**1c**).

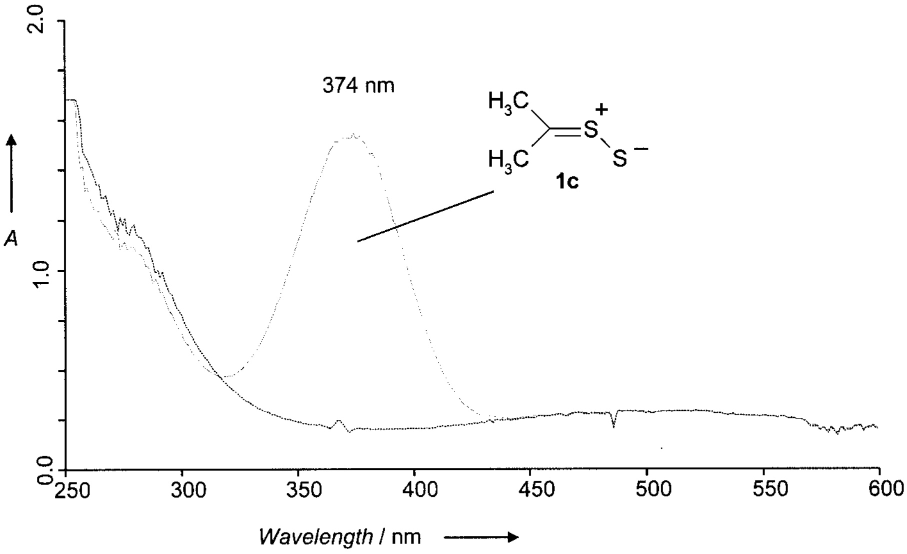


Figure 3. Solid line: UV/Vis spectrum of matrix-isolated (Ar, 10 K) pyrolysis products of tetramethyltrithiolane (**3c**); dotted line: after subsequent irradiation (4 min, $\lambda$ = 366 nm).

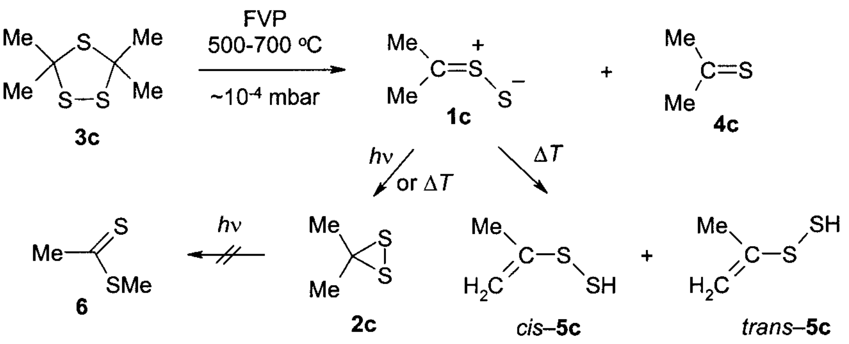


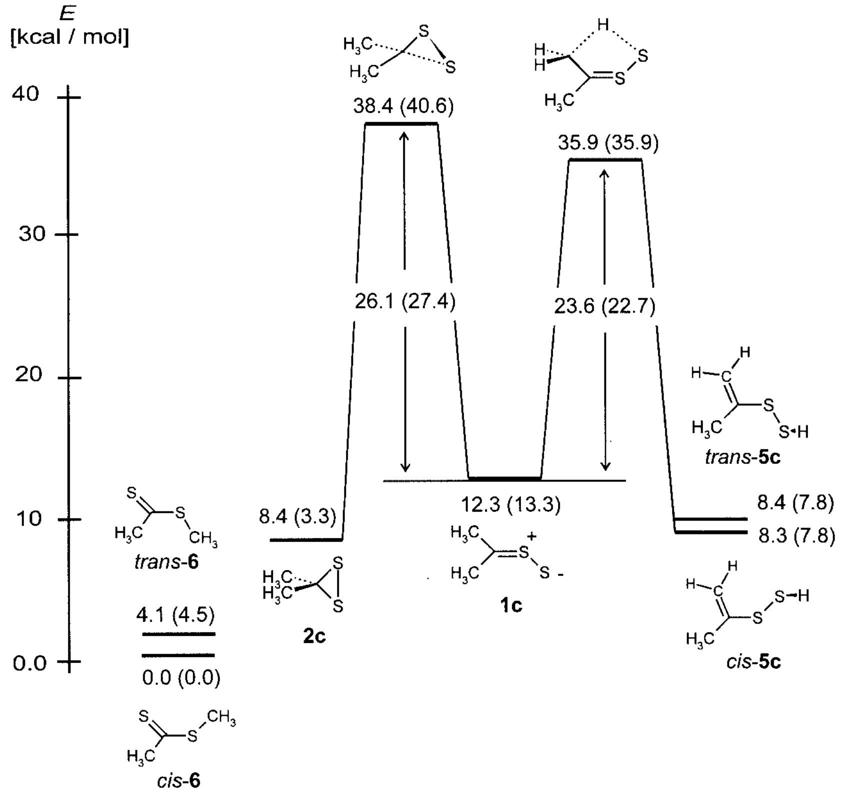
Table 1. Comparison of computed and experimental UV absorptions of **1a**, **1b**, and **1c**.

| | Experimental absorption maxima (Ar, 12 K) / nm | Computed first three electronic transitions (TD//B3LYP/6-311+G**) / nm (oscillator strength) |
|---|---|---|
| **1a** | 356 | 548 (0.0000), 347 (0.1556), 260 (0.048) |
| **1b** | 368 | *s-cis*: 505 (0.0001), 351 (0.1584), 258 (0.0031);<br>s-*trans*: 528 (0.0000), 366 (0.1779), 277 (0.0007) |
| **1c** | 374 | 494 (0.0002), 357 (0.1772), 278 (0.0010) |

It is worth mentioning that the reduction of the band intensity in the UV spectrum during the irradiation of dimethylsulfine **1c** was accompanied with the disappearance of the IR bands attributed to this compound. At the same time, as already discussed (Figure 2), the IR absorption bands assigned to **2c** gained intensity. Dithiiranes are reported to show a very weak n → σ* absorption in the visible region at ca. $\lambda_{\max}$ = 450 nm.[2] However, in our experiment no new absorption band was observed. Probably the intensity of the transition was too low for detection (Figure 3).

In contrast to the parent thiosulfine **1a** the dimethyl derivative **1c** does not undergo photoisomerisation to methyl dithioacetate **6**, which could be expected as the product of a migration of the methyl group. Moreover, the intensities of the absorption bands ascribed to **5c** did not increase during irradiation.

In order to understand the different behavior of **1a** and **1c** the pathways starting from **1c** were computationally analyzed using the *Gaussian* package of programs.[14a,14b] Cartesian coordinates, energies, and vibrational wavenumbers of all calculated compounds are collected in the Supporting Information. Eight stationary points of the $C_3H_6S_2$ potential energies surface were optimized by density functional theory calculations using the B3LYP hybrid functional with 6-311+G** basis set.[14a] Additionally coupled cluster single point energies [CCSD(T)/cc-pVDZ, values given in parentheses] were computed for each stationary point[14b] (Scheme 1). The results show that the *cis* rotamer of methyl dithioacetate (**6**) is the global minimum in energy. Dimethyldithiirane (**2c**) is 8.4 (3.3) kcal mol$^{-1}$ higher in energy, nearly the same energy level is found for the two rotamers of (propen-2-yl)disulfane (**5c**). The energy of dimethylthio-



Scheme 1. Computed relative energies of some $C_3H_6S_2$ isomers and of the transition states connecting **1c** with **2c** and **5c**; [B3LYP/6-311+G**, CCSD(T)/cc-pVDZ//B3LYP/6-311+G** in parentheses, both corrected by B3LYP zero-point vibrational energies].

sulfine (**1c**) is 3.9 (10.0) kcal mol$^{-1}$ higher than for the isomeric dithiirane **2c**.

Two transition states connecting **1c** with **2c** ($E_a$ = 26.1 kcal mol$^{-1}$) or **1c** with **5c** ($E_a$ = 23.6 kcal mol$^{-1}$) were found on B3LYP/6-311+G** level. Single point coupled cluster calculations [CCSD(T)/cc-pVDZ] yielded slightly different values (27.4 and 22.7 kcal mol$^{-1}$, respectively). Based on these computational results two competitive reactions leading to **2c** and **5c**, respectively, can be predicted in slight favor of the latter reaction. The energy for the retro [2+3]-cycloaddition of the precursor molecule **3c** leading to **1c** and **4c** is calculated to amount to 20.8 kcal/mol$^{-1}$. This value is slightly lower than the calculated activation energies for the two subsequent conversions of initially formed **1c**. In so far the experimentally established composition of the pyrolysate reflects the computational predictions.

### *Methylthiosulfine*

In extension of the study on alkyl-substituted thiosulfines the flash vacuum pyrolysis of 3,5-dimethyl-1,2,4-trithiolane (**3b**) (mixture of *cis* and *trans* isomers) was performed at 700 °C. In analogy to the experiment with **3a**, the product was condensed on a CsI window cooled to 10 K and its composition was analyzed by the IR spectrum. The most intense absorption bands, localized at 1356.7 and 1359.5 cm$^{-1}$, proved the presence of thioacetaldehyde **4b**.[15] When the matrix was irradiated for a short time (1 min) with 366-nm light and subsequently with light of the wave-

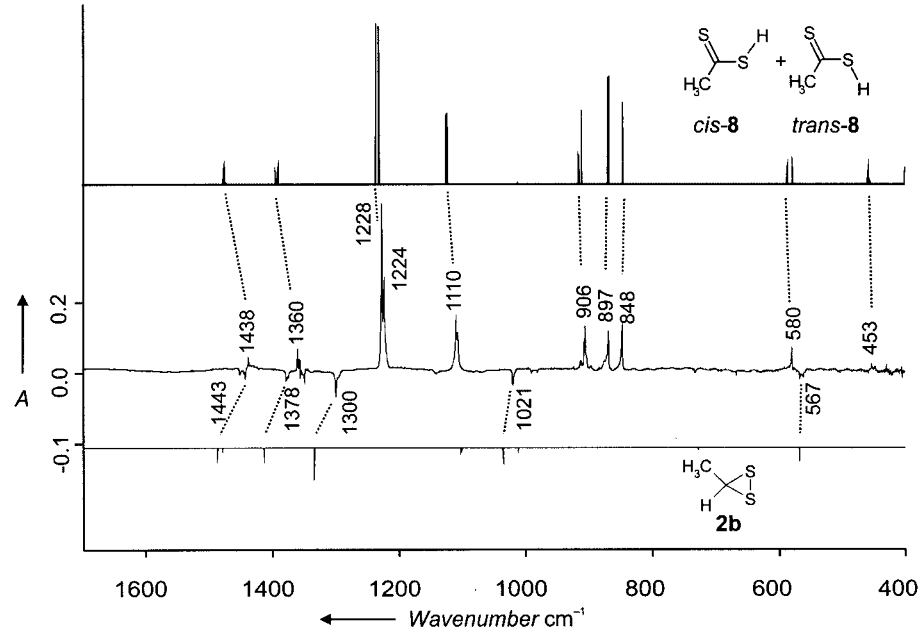
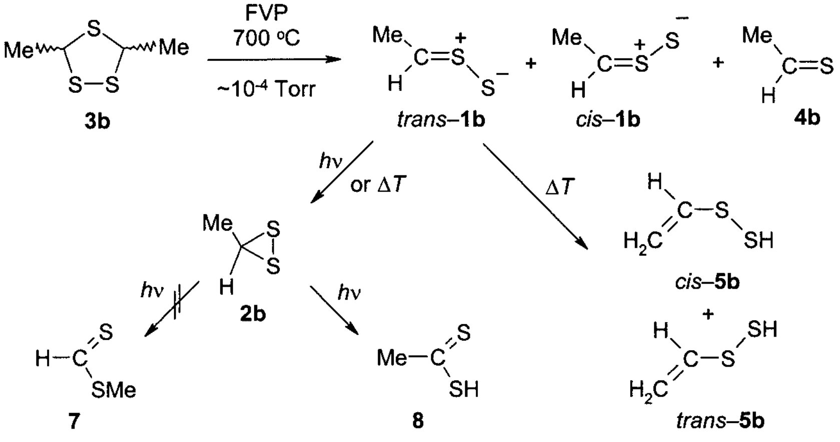
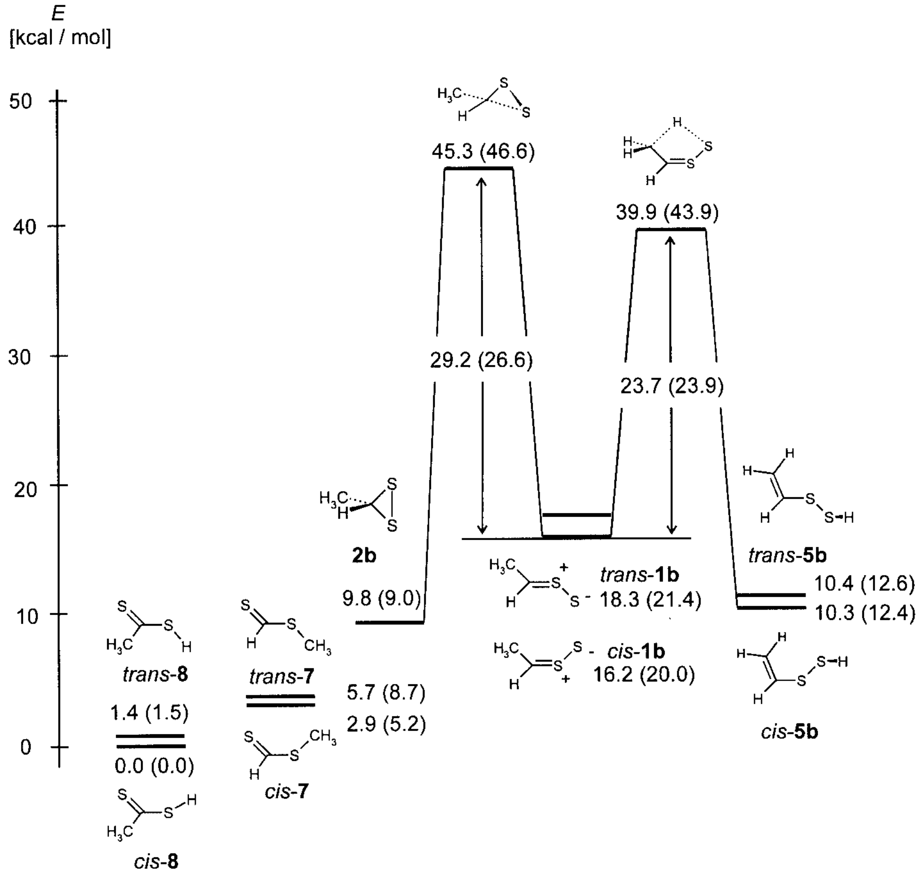


Figure 4. Middle: difference IR spectrum (B–A) monitoring the photo-rearrangement of dithiiran **2b** (negative bands) into dithioacetic acid (**8**) (positive bands). Spectrum A: argon matrix of the pyrolysis products of dimethyltrithiolane (**3b**), irradiated for 7 min at $\lambda$ = 366 nm; spectrum B: recorded after additional 3.5 h irradiation with $\lambda$ > 310 nm. Top: computed (B3LYP/6-311+G**) spectra of a 1:1 mixture of *cis*- and *trans*-**8**. Bottom: computed (B3LYP/6-311+G**) IR spectrum of methyldithiiran (**2b**).



length >310 nm new absorptions appeared in the IR spectrum at 1228 and 1224 cm$^{-1}$, which indicate the formation of *s-cis-* and *s-trans*-dithioacetic acid (**8**) via rearrangement of primarily generated methyldithiirane **2b** (Figure 4).

Methyldithiirane **2b** could also be detected in the original spectrum (before irradiation), as evidenced by the presence of its bands at 1300 and 567 cm$^{-1}$. In addition, relatively strong absorptions at 1594.5 and 955.4 cm$^{-1}$ proved the



Scheme 2. Computed relative energies of some $C_2H_4S_2$ isomers and of the transition states connecting **1b** with **2b** and **5b**; [B3LYP/6-311+G**, CCSD(T)/cc-pVDZ//B3LYP/6-311+G** in parentheses, both corrected by B3LYP zero-point vibrational energies].

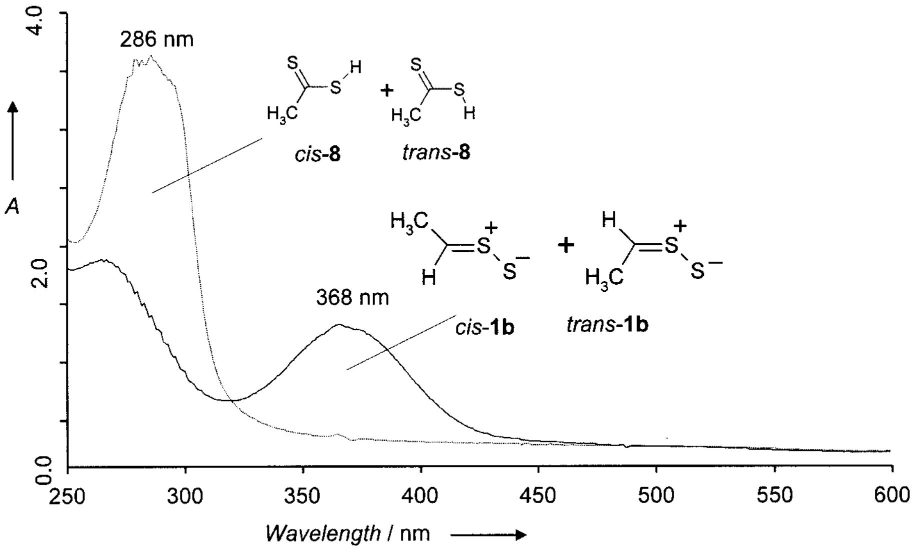


Figure 5. Solid line: UV/Vis spectrum of matrix isolated (Ar, 10 K) pyrolysis products of dimethyltrithiolane (**3b**); dotted line: after irradiation (1 min, $\lambda$ = 366 nm, 30 min, $\lambda$ > 310 nm).

presence of *s-cis-* and *s-trans*-vinyldisulfane **5b**. This set of bands did not change upon irradiation, indicating that the vinyldisulfanes **5b** originate from a thermally and not photochemically induced [1,4]-H shift in **1b**.

The calculated $C_2H_4S_2$ potential energy surface (Scheme 2) shows that the relative energies of the relevant minima and transition states are very similar to those discussed for conversions of dimethylthiosulfine (**1c**) (Scheme 1).

In analogy to the pyrolysis of **3c**, the presence of methylthiosulfine (**1b**) in the product mixture of **3b** was evidenced by a strong UV absorption at $\lambda_{\max}$ = 368 nm (Figure 5). This absorption disappeared completely upon short irradiation with 366 nm-light (compare IR results discussed above). Longer irradiation with $\lambda > 310$ nm led to a new absorption, which can be assigned to dithioacetic acid (**8**) ($\lambda_{\max}$ = 286 nm).

Parallel to the dimethyl series in no case a photo-rearrangement of **2b** into methyl dithioformate **7** was observed.

### *Studies in Solution*

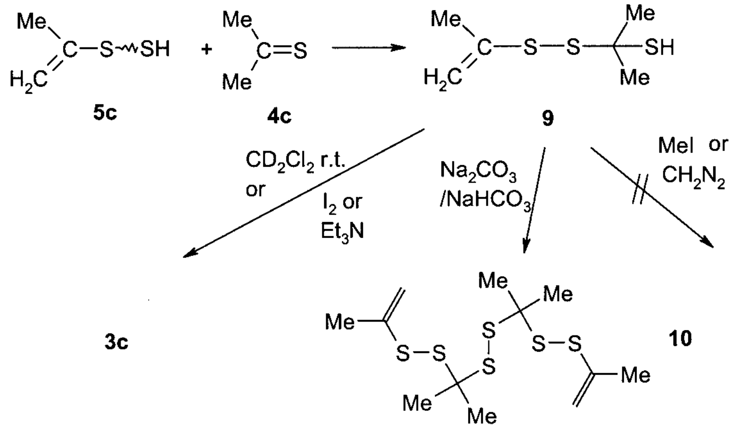
The argon matrix experiments indicated that the main product formed upon vacuum pyrolysis of 3,3,5,5-tetramethyl-1,2,4-trithiolane (**3c**) is (propen-2-yl)disulfane **5c**, which is the product of a [1,4]-H shift in dimethyl thiosulfine (**1c**) (Figure 1). This procedure was expanded to a larger scale by pyrolyzing **3c** without a carrier gas and condensing the products at 77 K (liquid nitrogen). The layer condensed on the cold surface was orange, indicating the presence of monomeric thioacetone (**4c**). After completion of the pyrolysis a portion of dichloromethane was condensed onto the cold surface and the condensed layers were warmed up slowly. At around –95 °C the condensed material became liquid and dropped directly into a pre-cooled NMR tube. After sealing of the tube the $^1$H and $^{13}$C NMR were taken at low temperature (–80 °C). The characteristic signals for thioacetone were found in the $^{13}$C NMR spectrum at $\delta$ = 255.6 (C=S) and 42.2 (2 Me), showing satisfactory agreement with the literature data.[16] Three other signals at $\delta$ = 140.7 ($CH_2$=*C*), 108.8 (*C*$H_2$=C) and 20.9 ($CH_3$) revealed the presence of (propen-2-yl)disulfane **5c**. No significant changes in the $^{13}$C NMR spectra were observed when the temperature was raised to –36 °C.

After 1 day at room temperature the spectrum was taken again. Astonishingly, new signals at $\delta$ = 77.7 and 31.4 revealed the reformation of the starting molecule, namely 1,2,4-trithiolane **3c**. A plausible explanation for the reverse process **5c** + **4c** → **3c** might be the following: disulfane **5c** adds in solution to the C=S group of thioacetone yielding disulfide **9**, which then cyclizes to give **3c**.

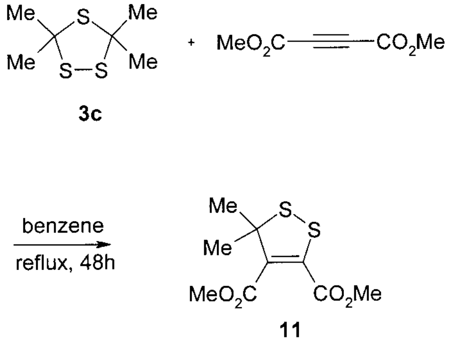
In another experiment the pyrolysate was condensed at –78 °C (dry ice/acetone). In contrast to the experiment discussed before the collected material was colorless, indicating the absence of free thioacetone (**4c**). The $^{13}$C NMR spectrum (room temperature) showed signals at $\delta$ = 141.8 ($CH_2$=*C*), 111.6 ($CH_2$=*C*), 56.2 ($C_q$), 32.8 (2 $CH_3$) and 21.6 ($CH_3$). In the $^1$H NMR spectrum two olefinic geminal H atoms were found at $\delta$ = 5.32 (q) and 5.09 (q), respectively. These spectroscopic data revealed the presence of adduct **9** as the sole product in the solution. Unexpectedly, this compound was detected even after 24 h at room temperature. So, under these conditions no ring closure **9** → **3c** had taken place. That means, in the other experiment this process must have been catalyzed. Indeed, when a solution of **9** was treated at room temperature with iodine or triethylamine a fast cyclization of **9** to **3c** occurred.

Last but not least it should be mentioned that an oxidative coupling of thiol **9** to disufide **10** can easily be achieved by adding a base, for instance by stirring a suspension between sodium carbonate and a solution of **9** at room temperature. It is worth of mentioning that attempted *S*-methylations of **9** using methyl iodide or diazomethane were in vain and in both cases steric shielding of the SH group seems to play the crucial role.

We also tried to trap dimethylthiosulfine (**1c**), the primarily formed fragment in the pyrolysis of trithiolane **3c**, before it isomerizes to disulfane **5c**. Therefore the thermolysis of **3c** was carried out in presence of dimethyl acetylenedicarboxylate (DMAD). The reagents were heated in boil-



ing benzene solution in the presence of an equimolar amount of DMAD for 48 h. The $^1$H NMR spectrum of the crude reaction mixture showed that the DAMD was almost completely consumed and new signals for MeO groups were observed at $\delta$ = 3.83 and 3.79 ppm, respectively. After chromatographic workup a yellow oil was obtained and the NMR spectroscopic data confirmed the formation of 1,2-dithiolane derivative **11**. This result confirms that thermal activation of **3c** leads to a retro-[2+3]-cycloaddition generating thioacetone *S*-sulfide **1c**, which can be trapped with a reactive dienophile such as DMAD. In the absence of any trapping reagent trithiolane **3c** remained unchanged, even when heated 48 h in boiling benzene.



## Conclusions

Matrix-isolation spectroscopy in combination with quantum chemical calculations, a technique which has been used before for the first detection of the parent thiosulfine (**1a**),[3] can also be applied for the study of the methyl-substituted derivatives **1b** and **1c**. The conclusions drawn for **1a** can be completed by the following facts: a) If a methyl group is situated at the carbon atom as in **1b** or **1c** the preferred reaction is a [1,4]-H shift and a vinyldisulfane **5** is formed. b) Photochemical activation generates as in the case of **1a** the corresponding dithiiranes **2**. c) Upon irradiation **2b** and **2c** do not undergo methyl migration to give methyl dithiocarboxylate **6** or **7**; in **2b** only a hydrogen atom is shifted to the neighbored sulfur atom resulting in **8**. d) Methyl substitution stabilizes the involved species to such an extent that the matrix results can be imaged by preparative runs in solution and at higher temperatures.

## Experimental Section

**Matrix Studies:** The cryostat for matrix isolation was a helium closed-cycle refrigeration system (compressor unit RW2 with coldhead base unit 210 and extension module ROK) from Leybold. The matrix IR spectra were measured using a FT-IR instrument IFS 85 or IFS 55 from Bruker, the UV/Vis spectra were taken with a Hewlett–Packard HP 8453 diode-array spectrophotometer. The light sources used were a mercury high-pressure lamp (HBO 200 from Osram) with a monochromator (Bausch and Lomb) and a mercury low-pressure spiral lamp with a Vycor filter (Gräntzel).

**Studies in Solution:** IR spectra were measured with a Nexus FT-IR spectrometer. Mass spectroscopic data were obtained by using a Finnigan MAT 95 or Varian MAT-112S, which was operated in the EI mode. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker 200 MHz instrument in $CDCl_3$ using TMS as an internal standard. In the case of the $^{13}$C NMR spectra, multiplicity of the corresponding signals were established based on the DEPT experiment. Compounds **9**, **10**, and **11** were oily substances which slowly decomposed during attempted purification or storage at room temperature; therefore the convincing identification of their relatively simple structures was achieved based on the spectroscopic data only; no correct elemental analyses could be obtained.

**Starting Materials:** Unseparated mixture of *cis*- and *trans*-3,5-dimethyl-1,2,4-tritholanes (*cis*-**3b** and *trans*-**3b**) and 3,3,5,5-tetramethyl-1,2,4-trithiolane (**3c**) were prepared from diisobutylamine, sulfur, sulfur hydrogen and acetaldehyde or acetone, respectively, following Asinger's procedure.[17]

**Flash Vacuum Pyrolysis (FVP) of 3,3,5,5-Tetramethyl-1,2,4-trithiolane (3c):** Trithiolane **3c** (300 mg, 1.67 mmol) was pyrolyzed at 700 °C in a FVP apparatus (cold finger at –78 °C). The almost colorless oil was washed from the cold finger with $CH_2Cl_2$. The collected product was $^1$H NMR pure and could be identified as [(isopropen-2-yl)disulfanyl]propane-2-thiol (**9**); 280 mg (93%). $^1$H NMR: $\delta$ = 5.32 (q, $^4J$(H,H) = 0.7 Hz, 1 H), 5.09 (q, $^4J$(H,H) = 1.4 Hz, 1 H), 2.47 (m, $^4J$(H,H) = 0.8 Hz, 1 H, exchangeable with $D_2O$), 2.04 (dd, $^4J$(H,H) = 1.4, $^4J$(H,H) = 0.7 Hz, 3 H), 1,68 (d, $^4J$(H,H) = 0.8 Hz, 6 H). $^{13}$C NMR: $\delta$ = 141.2 (s), 111.4 (t), 56.0 (s), 32.6 (q), 21.6 (q). IR (film): $\tilde{\nu}$ [cm$^{-1}$] = 3081, 2965, 2919, 2549 (SH), 1624, 1611. MS (EI): *m*/*z* (%): 180 [M$^+$, 19], 106 (23), 74 (26), 59 (100).

**Reaction of 9 with $Na_2CO_3$/$NaHCO_3$:** A solution of **9** (200 mg, 1.1 mmol) in THF (5 mL) was stirred with 0.5 g of a 1:1 mixture of $Na_2CO_3$ and $NaHCO_3$ for 24 h. The suspension was filtered through silica gel and the solvent was removed, yielding disulfide **10** as a slightly yellow oil; 150 mg (0.42 mmol, 76%). $^1$H NMR: $\delta$ = 5.35 (q, $^4J$(H,H) = 0.5 Hz, 1 H), 5.13 (q, $^4J$(H,H) = 1.4 Hz, 1 H), 2.03 (m, 3 H), 1.64 (s, 6 H). $^{13}$C NMR: $\delta$ = 141.4 (q), 111.8 (s), 63.1 (s), 28.7 (q), 21.6 (q). IR (film): $\tilde{\nu}$ [cm$^{-1}$] = 3083, 2962, 2918, 1624, 1611. MS (EI): *m*/*z* (%): 147 (100) [$H_2C=C(Me)–S–S–CMe_2$]$^+$, 179 (26) [$H_2C=C(Me)–S–S–CMe_2–S$]$^+$, 211 (10) [$H_2C=C(Me)–S–S–CMe_2–S–S$]$^+$, 253 (15) [$H_2C=C(Me)-S–S–CMe_2–S–S–CMe_2$]$^+$, 285 (2) [$H_2C=C(Me)-S–S–CMe_2–S–S–CMe_2–S$]$^+$.

**Reaction of Dimethylthiosulfine (1c) with Dimethyl Acetylenedicarboxylate (DMAD):** A solution of trithiolane **3c** (90 mg, 0.5 mmol) and DMAD (80 mg, 0.5 mmol) in benzene (5 mL) was refluxed for 48 h. The solvent was removed and the residue purified using preparative thin layer chromatography ($SiO_2$, $CH_2Cl_2$/hexane, 1:1). Pure dimethyl 5,5-dimethyl-5*H*-1,2-dithiole-3,4-dicarboxylate (**11**) was obtained as a yellow oil; 75 mg (0.3 mmol, 61%). $^1$H NMR: $\delta$ = 3.83 (s, 3 H), 3.79 (s, 3 H), 1.67 (s, 6 H). $^{13}$C NMR: $\delta$ = 164.9 (s), 161.1 (s), 142.1 (s), 137.0 (s), 66.4 (s), 53.0 (q), 52.6 (q). IR (film): $\tilde{\nu}$ [cm$^{-1}$] = 2953 (m), 1736 (vs), 1608 (m), 1456 (m), 1434 (s), 1262 (vs), 1213 (s), 1075 (s), 1030 (s). MS (EI): *m*/*z* (%): 248 [M$^+$, 31], 233 (100), 201 (23), 173 (18).

**Reaction of 9 with $I_2$:** An excess of $I_2$ was added to a solution of **9** (90 mg, 0.5 mmol) in $CDCl_3$ (0.5 mL). After standing overnight at room temperature the solvent was removed. The $^1$H NMR spectrum of the residue showed no starting material but only a singlet at 1.88, which had to be assigned to **3c**.

**Reaction of 9 with $CH_2N_2$ or MeI:** $CH_2N_2$ in petroleum ether was added to **9** (90 mg, 0.5 mmol) at 0 °C. After standing at room temp. for 2 h and removal of the solvent, only unreacted **9** was found.

The same negative result was observed when MeI was stirred with **9** (90 mg, 0.5 mmol) in THF (5 mL) at room temp. for 24 h.

**Reaction of 9 with $Et_3N$:** To the solution of **9** (90 mg, 0.5 mmol) in $CH_2Cl_2$ (5 mL) at room temp. two drops of $Et_3N$ were added. The colour of the solution changed into slight yellow. Solvent was removed. The $^1H$ NMR of the residue showed no starting material but only a singlet for **3c** at 1.88.

**Supporting Information** (see also the footnote on the first page of this article): Additional computational results, energies, Cartesian coordinates, and vibrational frequencies of all optimized structures are available in the Supporting Informations.

## Acknowledgments

Support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. G. Mloston and J. Romanski acknowledge financial support by the Polish State Committee for Scientific Research (Grant KBN No. 4 T09A 046 25). H. Petzold acknowledges financal support by DAAD (PKZ D/04/11451, H. P.).

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Received: February 22, 2006