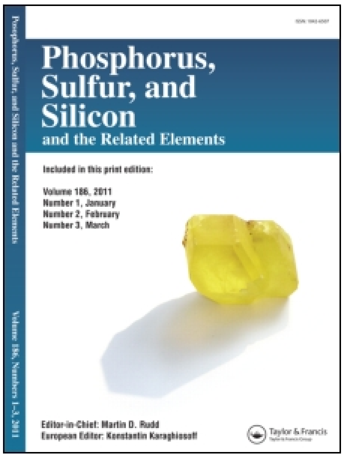

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# SULFUR COMPOUNDS 141[1]: SYSTEMATIC BUILD-UP OF ORGANIC POLYSULFANES - SYNTHESIS AND SPECTRA OF THE CYCLIC HEPTA- AND OCTASULFANES OF NORBORNANE, $C_7H_{10}S_7$ AND $C_7H_{10}S_8$

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# SULFUR COMPOUNDS 141[1]: SYSTEMATIC BUILD-UP OF ORGANIC POLYSULFANES - SYNTHESIS AND SPECTRA OF THE CYCLIC HEPTA- AND OCTASULFANES OF NORBORNANE, $C_7H_{10}S_7$ AND $C_7H_{10}S_8$

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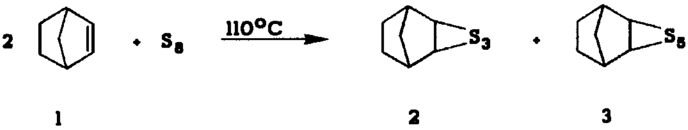
The cyclic polysulfanes exo-3,4,5,6,7,8,9-heptathiatricyclo[9.2.1.$0^{2,10}$]tetradecane ($C_7H_{10}S_7$) and exo-3,4,5,6,7,8,9,10-octathiatricyclo[10.2.1.$0^{2,11}$]-pentadecane ($C_7H_{10}S_8$) have been prepared from the corresponding trisulfane $C_7H_{10}S_3$ by chlorination resulting in the two sulfenylchlorides $C_7H_{10}(SCl)_2$ and $C_7H_{10}(SCl)(S_2Cl)$ which react with $(C_5H_5)_2TiS_5$ to yield the title compounds in good yields. Similarly, $C_7H_{10}S_5Cl_2$ was obtained from $C_7H_{10}S_5$ and $Cl_2$ and yielded $C_7H_{10}S_{10}$ on treatment with $(C_5H_5)_2TiS_5$. The hepta- and octasulfanes form pale-yellow microcrystals which have been characterized by UV, mass, Raman, and $^1H$ NMR spectroscopy. The retention time of $C_7H_{10}S_n$ molecules in reversed-phase HPLC is a function of the number of sulfur atoms ($n = 3 \ldots 12$).

*Key words:* organic polysulfides; norbornane derivatives; sulfur transfer reaction; HPLC; titanocene derivatives

## INTRODUCTION

Norbornene **1** (2-bicyclo[2.2.1]heptene, $C_7H_{10}$) is known to react with elemental sulfur thermally to give the tricyclic sulfanes **2** and **3**[2,3]:



Scheme 1

The reaction is catalyzed by amines and use of pyridine as a solvent and $NH_3$ and DMF as catalysts provides **2** (exo-3,4,5-trithiatricyclo[5.2.1.$0^{2,6}$]decane) and **3** (exo-3,4,5,6,7-pentathiatricyclo[7.2.1.$0^{2,8}$]dodecane) in good yields and in a molar ratio of 3.5:1.[3] The molecular structure of **3** has been shown by X-ray crystallography to be of $C_s$ symmetry with the heterocycle in a chair conformation and SS bond lengths of between 203.4 and 206.6 pm.[4]

In connection with the chemistry of sulfur cement[5] which is made by heating cyclic olefins with elemental sulfur and which is believed to contain long-chain

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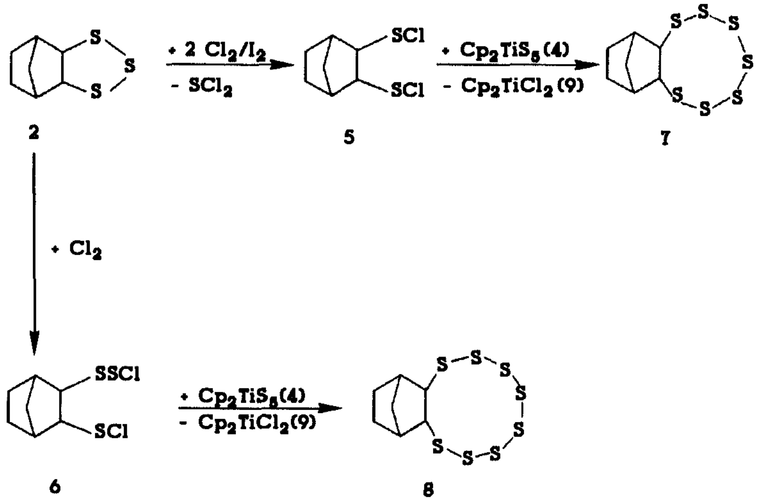
polysulfanes ($-S_x$-R-$S_y$-R-$S_z$-) we have been interested in the synthesis of sulfur-rich cyclic norbornane polysulfides which obviously cannot be obtained by simple heating of norbornene and sulfur. We report here a new synthesis for cyclic polysulfanes which makes use of the sulfur-transfer reagent bis($\eta^5$-cyclopentadienyl)titanium pentasulfide, $Cp_2TiS_5$ (**4**). The latter compound has been used very successfully for the preparation of sulfur-rich inorganic homo- and heterocycles[6] and chain-like polysulfanes.[7] Since **4** reacts with sulfenylchlorides we have transformed **2** into the SCl compounds **5** and **6** which were reacted with **4** to give the new compounds **7** and **8**:



Scheme 2:

## RESULTS AND DISCUSSION

### *Synthesis of $C_7H_{10}S_7$*

The chlorination of the trithiolane **2** with elemental chlorine in $CCl_4$ solution at 0°C and in the presence of traces of iodine was found to yield the bis(sulfenylchloride) **5** in quantitative yield as an orange oil. This compound has been used without further purification for the sulfur-transfer reaction with **4** which proceeds in $CS_2$ solution at 20°C. **4** has to be applied in slight excess to quantitatively remove all sulfenylchloride from the solution. After removal of the precipitated titanocene dichloride, $Cp_2TiCl_2$ (**9**), hexane was added to the solution whereupon the heptasulfane **7** (exo-3,4,5,6,7,8,9-heptathiatricyclo[9.2.1.$0^{2,10}$]tetradecane) precipitated on cooling to $-78$°C as a pale-yellow powder of m.p. 80°C (dec.). The EI mass spectrum of **7** shows the molecular ion at $m/z = 318$, the exo position of the sulfur atoms follows from the 400 MHz $^1$H-NMR spectrum which has been assigned by comparison with that of **2**[3] (Table I). The 10 observed signals can be assigned to two conformers of **7** (A and B) on the basis of their intensities assuming that three signals overlap at 1.69 ppm. On this basis there are two sets of 6 signals each to be assigned to the protons $H_a$ . . . $H_f$ as shown in Figure 1 and Table I. This

TABLE I

$^1$H-NMR spectrum (400 mHz; $CDCl_3$) of $C_7H_{10}S_7$ (**7**) and assignment to the hydrogen atoms *a* . . . *f* of two conformers of $C_s$ symmetry (see Figure 1); *d* = doublet, *m* = multiplet

| Chem. Shift (ppm) | Signal Type | Coupling Constant (Hz) | Assignment | Conformer |
|---|---|---|---|---|
| 3.95 | *m* | — | *a* | *A* |
| 3.66 | *d* | 2 | *a* | *B* |
| 2.68 | *m* | — | *b* | *B* |
| 2.45 | *m* | — | *b* | *A* |
| 1.72 | *m* | — | *e* | *B* |
| 1.69 | *m* | — | *d* | *A* and *B* |
| | | | *e* | *A* |
| 1.40 | *dm* | 8 | *c* | *A* |
| 1.34 | *dm* | 11 | *f* | *B* |
| 1.27 | *m* | — | *c* | *B* |
| 1.20 | *dm* | 11 | *f* | *A* |

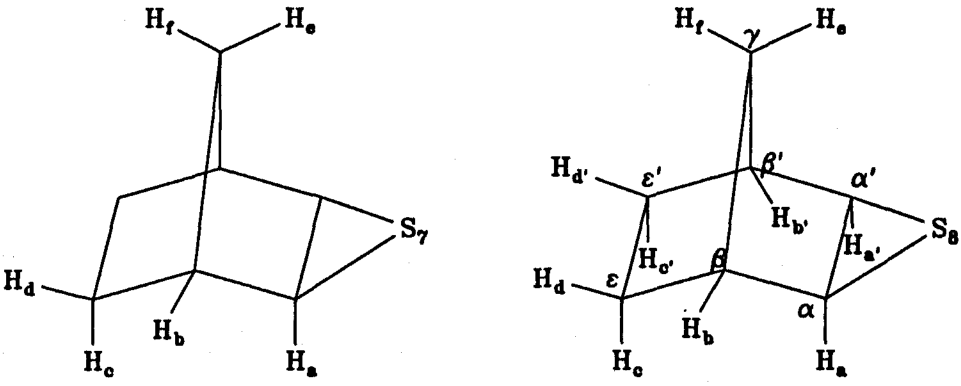


FIGURE 1 Labeling of hydrogen and carbon atoms in $C_7H_{10}S_7$ (symmetry $C_s$; left) and $C_7H_{10}S_8$ (symmetry $C_1$; right).

assignment implies that the nine-membered $C_2S_7$ rings of both conformers are of $C_s$ symmetry which seems reasonable considering the above mentioned structure of **3**. Subsequent HPLC analysis[9] of the $CDCl_3$ solution of **7** used to measure the NMR spectrum showed only one substance peak proving that no decomposition had taken place during the NMR analysis. The peak areas of protons a and b (see Table I) provided the molar ratio of conformers A and B as 7:2. The most likely conformations of A and B are shown in Figure 3. These structures have been adapted from the results of density functional calculations of the $S_9$ molecule.[8] In its ground state $S_9$ is of $C_2$ symmetry but the two conformations of $C_s$ symmetry shown in Figure 3 are only slightly less stable and are of almost equal energy.[8] At present it seems however impossible to decide which conformer of **7** (A or B) represents which structure of Figure 3.

UV, Raman, and infrared spectra also support the composition and structure of **7**. The SS stretching vibrations show up in the Raman spectrum as a cluster of six signals between 417 and 493 cm$^{-1}$. Both in the solid state and in solution **7** de-

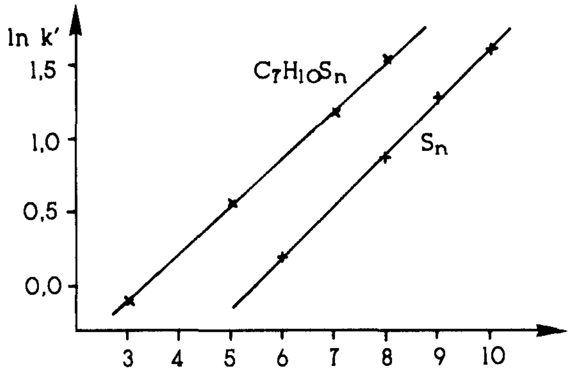


FIGURE 2 Retention behaviour of cyclic sulfur rings ($S_n$) and norbornane polysulfanes ($C_7H_{10}S_n$). Plotted is the logarithm of the capacity factor $k'$ versus the number of sulfur atoms in the molecule ($n_s$). The correlation coefficients for both lines are better than 0.999.

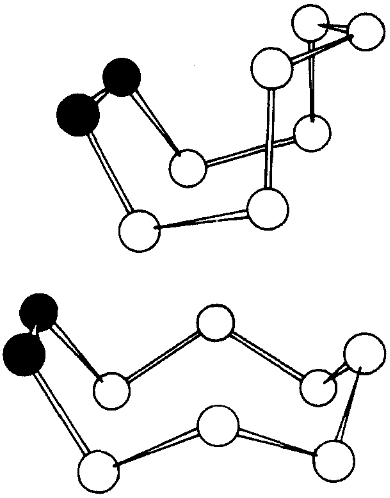


FIGURE 3 Likely conformations of the nine-membered $C_2S_7$ rings in the two conformers of $C_7H_{10}S_7$ (the carbon atoms are on the left; the rings are of $C_s$ symmetry).

composes at 20°C in diffuse daylight within several days with formation of **2**, **3**, and $S_8$. In addition, small amounts of other $C_7H_{10}S_n$ molecules with $n = 8, 9, 10, 11$, and 12 were detected by HPLC. These results show that the decomposition of $C_7H_{10}S_n$ into $S_8$ and $C_7H_{10}S_m$ ($m < n$) proceeds stepwise as follows:

$$2\,C_7H_{10}S_7 \rightleftharpoons C_7H_{10}S_5 + C_7H_{10}S_9$$

$$2\,C_7H_{10}S_7 \rightleftharpoons C_7H_{10}S_3 + C_7H_{10}S_{11}$$

$$C_7H_{10}S_{11} \rightleftharpoons C_7H_{10}S_3 + S_8$$

$$2\,C_7H_{10}S_9 \rightleftharpoons C_7H_{10}S_7 + C_7H_{10}S_{11}$$

etc.

Species with 2, 4, and 6 sulfur atoms were not observed by HPLC which may be explained by their high reactivity. At −60°C solid **7** did not decompose within weeks.

The fragmentation pattern of **7** in the EI-mass spectrum (70 eV; sample temperature 70°C) is characterized by the loss of $S_n$ units ($n = 2, 3, 4, 5, 6, 7$) as is typical also for homocyclic sulfur molecules[10] (see Table II).

### *Synthesis of* $C_7H_{10}S_8$

Chlorine treatment of **2** at 20°C in $CCl_4$ without addition of iodine resulted in the cleavage of only one SS bond and formation of **6** within 10 min. **6** was isolated as orange oil in seemingly quantitative yield and was identified by EI mass spectrometry (molecular ion at $m/z = 260$). Under the above conditions **6** reacts only slowly with an excess of chlorine to give **5**.

As expected, **6** reacts at 0° to 20°C in $CS_2$ or $CH_2Cl_2$ solution rapidly with **4** to give the novel octasulfane **8** which was obtained as almost colorless microcrystalline powder. This reaction can best be monitored by reversed-phase HPLC which shows **8** and **9** as the major products. The low isolated yield of **8** (4%, not optimized) results from the difficulties with the separation of **8** from **9**. Exo-3,4,5,6,7,8,9,10-octathiatricyclo[10.2.1.$0^{2,11}$]pentadecane (**8**) melts at 93°C almost undecomposed but heating to 140°C for 10 min resulted in a quantitative decomposition to **2**, **3**, and $S_8$.

The HPLC retention times ($t_r$) of **2**, **3**, **7**, and **8** systematically depend on the number of sulfur atoms ($n_s$) and a linear correlation is obtained when the logarithm of the capacity factor $k'$ ($k' = t_r - t_o/t_o$; $t_o$ = dead time) is plotted versus $n_s$ (see Figure 2). Table III gives the retention data including the retention indices[11] which are independent of the flow and of the apparatus (but do depend on the eluent). This technique then allows the identification of new members of the homologous series of $C_7H_{10}S_n$ molecules simply from their retention time. When the HPLC apparatus is connected to a diode-array UV detector the UV-VIS absorption spectra of the freshly separated norbornane polysulfides can be recorded on-line.[12] In this way the spectra of **2**, **3**, **7**, and **8** given in Figure 4 have been obtained.

TABLE II

Mass spectrum of $C_7H_{10}S_7$ (**7**) (EI, 70 eV; sample at 70°C)

| m/z | Rel. Intensity | Assignment |
|---|---|---|
| 318 | 7.6 | $M^+$ |
| 254 | 7.1 | $M^+$-$S_2$ |
| 224 | 10.1 | $S_7^+$ |
| 222 | 8.1 | $M^+$-$S_3$ |
| 190 | 100.0 | $M^+$-$S_4$ |
| 158 | 55.6 | $M^+$-$S_5$ |
| 126 | 67.2 | $M^+$-$S_6$ |
| 97 | 36.3 | $HS_3^+$ |
| 93 | 70.0 | $C_7H_9^+$ |
| 77 | 42.6 | $C_6H_5^+$ |
| 66 | 95.7 | $C_5H_6^+$ |

TABLE III

Retention data of sulfur rings and norbornane polysulfanes under identical conditions; eluent methanol, dead time 1.35 min. The retention indices (RS) of $S_n$ molecules are defined as 100 · $n_s$ ($n_s$ = number of S atoms), the RS values of other molecules are related to those of the $S_n$ molecules and therefore independent of the chromatographic apparatus[11]

| Substance | $t_r$ | $k'$ | RS |
|---|---|---|---|
| $S_6$ | 3.11 | 1.30 | 600 |
| $S_8$ | 4.71 | 2.49 | 800 |
| $S_9$ | 6.30 | 3.67 | 900 |
| $S_{10}$ | 8.09 | 4.99 | 1000 |
| $C_7H_{10}S_3$ | 2.67 | 0.97 | 515 |
| $C_7H_{10}S_5$ | 3.84 | 1.84 | 703 |
| $C_7H_{10}S_7$ | 5.81 | 3.30 | 875 |
| $C_7H_{10}S_8$ | 7.55 | 4.59 | 972 |

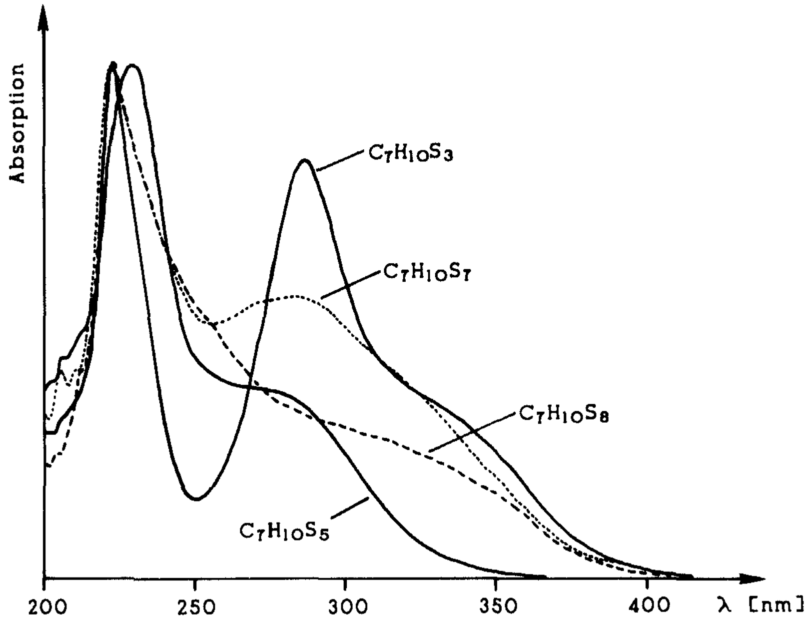


FIGURE 4 UV absorption spectra of the four cyclic norbornane polysulfanes $C_7H_{10}S_n$ (with $n$ = 3, 5, 7, and 8 dissolved in methanol). The spectra have been recorded by a diode-array detector and have been normalized (equal peak heights at 225 ± 3 nm). Peaks and shoulders (sh): **2**: 222, 284; **3**: 228, 276 (sh); **7**: 222, 284; **8**: 222, 300 (sh) nm.

The mass spectrum of **8** (70 eV, sample temperature 140°C) does not show a peak for the molecular ion but the heaviest ion detected is $S_{10}^+$. Besides $S_{10}^+$ the fragment ions $S_n^+$ ($n$ = 8, 7, 6, 5), $C_7H_{10}S_5^+$, $C_7H_{10}S_3^+$, and $C_7H_{10}S^+$ were detected which indicates that **8** had either partly decomposed prior to evaporation or was not stable under EI conditions. The following decomposition reactions may have taken place during heating:

$$C_7H_{10}S_8 \rightarrow C_7H_{10}S_3 + S_5$$

$$C_7H_{10}S_8 + S_5 \rightarrow C_7H_{10}S_3 + S_{10}$$

$$C_7H_{10}S_8 \rightarrow C_7H_{10}S_5 + S_3$$

$$C_7H_{10}S_8 + S_5 \rightarrow C_7H_{10}S_5 + S_8$$

$$C_7H_{10}S_8 + S_3 \rightarrow C_7H_{10}S_3 + S_8$$

Both the 400 MHz $^1$H-NMR and the $^{13}$C spectra show that **8** has no mirror plane but must be unsymmetrical (see Table IV). There are seven signals in the $^{13}$C spectrum (**2** and **3** show only four signals each)[3] and ten peaks of equal intensity in the $^1$H-NMR spectrum; with other words all carbon atoms and all hydrogen atoms are magnetically non-equivalent. The assumed structure of **8**, however, follows mainly from the synthesis. The molecule must contain a ten-membered $C_2S_8$ ring which may be compared to the cyclo-$S_{10}$ molecule which is of $D_2$ symmetry.[13] If any two neighboring S atoms in $S_{10}$ are substituted by C the resulting $C_2S_8$ ring will be of $C_1$ or $C_2$ symmetry but the whole $C_7H_{10}S_8$ molecule can only be of $C_1$ symmetry. It is therefore understandable that no two hydrogen atoms or two carbon atoms are equivalent.

### *Attempted Synthesis of $C_7H_{10}S_{10}$*

From the above it follows that each norbornane polysulfide can be used as starting material for a new chlorination and sulfur transfer reaction. Starting from $C_7H_{10}S_5$ it should be possible to synthesize $C_7H_{10}S_{10}$; Equation (2 and 3):

$$C_7H_{10}S_5(\mathbf{3}) + Cl_2 \rightarrow C_7H_{10}(SCl)(S_4Cl) \text{ or } C_7H_{10}(S_2Cl)(S_3Cl) \tag{2}$$

$$C_7H_{10}S_5Cl_2(\mathbf{10}) + Cp_2TiS_5(\mathbf{4}) \rightarrow C_7H_{10}S_{10}(\mathbf{11}) + Cp_2TiCl_2 \tag{3}$$

It can easily be seen that cleavage of any SS bond of **3** by chlorine will result in two isomeric dichlorides $C_7H_{10}S_5Cl_2$ which, however, yield the same cyclic decasulfide **11** by reaction with **4**.

TABLE IV

$^1$H and $^{13}$C-NMR spectra of $C_7H_{10}S_8$ (**8**) and assignment to the atoms as labelled in Figure 1; shifts in ppm, *d* = doublet; sample dissolved in $CDCl_3$, frequency 270 MHz

| $^1$H NMR (most signals broad) | | $^{13}$C NMR ($^1$H decoupled) | |
|---|---|---|---|
| Chem. Shift | Assignment | Chem. Shift | Assignment |
| 4.35 (*d*; 2 Hz) | *a'* | 71.65 | $\alpha'$ |
| 3.52 | *a* | 53.95 | $\alpha$ |
| 2.83 | *b'* | 46.83 | $\beta'$ |
| 2.63 | *b* | 39.19 | $\beta$ |
| 2.37 (*d*; 11 Hz) | *e* | 35.16 | $\gamma$ |
| 1.64 (*d*; 11 Hz) | *f* | | |
| 2.12 | *d'* | 27.43 | $\varepsilon'$ |
| 1.74 (*d*; 8 Hz) | *c'* | | |
| 1.84 | *d* | 25.89 | $\varepsilon$ |
| 1.38 (*d*; 9 Hz) | *c* | | |

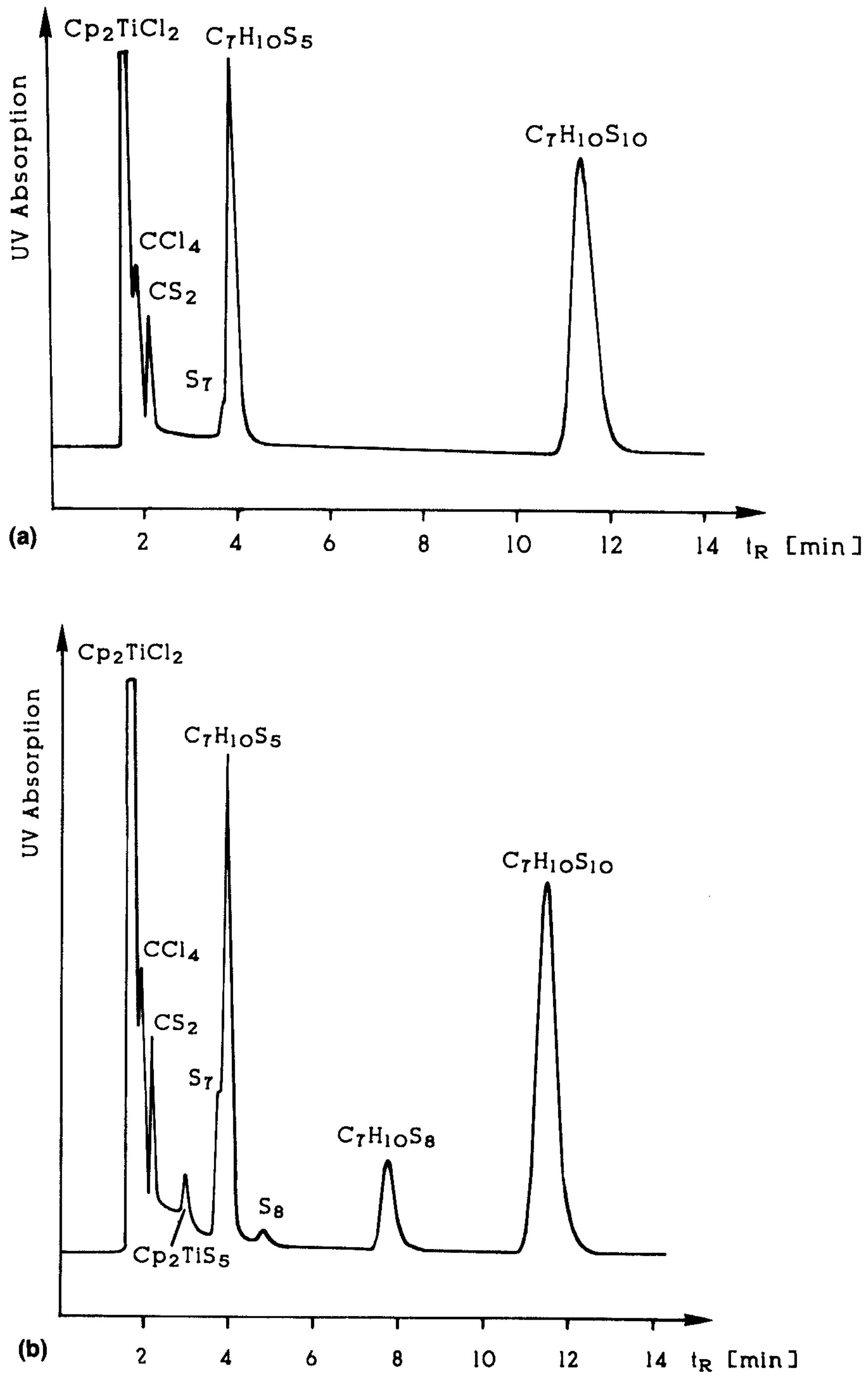


FIGURE 5 HPLC traces of the chlorination products of $C_7H_{10}S_5$ (dissolved in $CCl_4$) after treatment with $Cp_2TiS_5$ (dissolved in $CS_2$). Molar ratio $Cl_2$:$C_7H_{10}S_5$ = 1:2. Top (a): chlorination for 5 min; bottom (b): for 3 h. Eluent: methanol, stationary phase: octadecylsilane, particle size: 10 μm, column dimensions: 8 × 100 mm, detector wavelength: 254 nm.

It was found that **3** reacts slower with chlorine than **2** does. After chlorination at 20°C for a few minutes followed by addition of a $CS_2$ solution of **4** the expected decasulfide could be detected by HPLC: there was one large peak near the retention time calculated for $C_7H_{10}S_{10}$ from the above mentioned linear relationship $\ln k' = a \cdot n_s + b$ (see Figure 5a). Extended treatment (3 h) of **3** with $Cl_2$ in $CCl_4$ solution resulted also in the formation of $C_7H_{10}S_3Cl_2$ from which $C_7H_{10}S_8$ (**8**) was obtained by reaction with **4**; Equation (4):

$$\left.\begin{matrix} C_7H_{10}(SCl)(S_4Cl) \\ C_7H_{10}(S_2Cl)(S_3Cl) \end{matrix}\right\} + Cl_2 \rightarrow C_7H_{10}(SCl)(S_2Cl) + S_2Cl_2 \qquad (4)$$

Since $S_2Cl_2$ reacts with **4** to give $S_7$ the chromatograms showed a peak for the latter molecule in addition; see Figure 5b. No attempts were made yet to isolate the $C_7H_{10}S_{10}$ from the solution.

## CONCLUSIONS

The results presented above show that organic cyclic polysulfanes may be synthesized by a systematic build-up of the sulfur-chain using titanocene pentasulfide as an $S_5$-transfer reagent. Controlled chlorination of a di-, tri-, tetra- or pentasulfane first yields the required bis(sulfenylchloride) to which then five sulfurs are added in exchange for the two chlorine atoms. In a similar fashion the sulfur allotropes cyclo-$S_{11}$ and cyclo-$S_{13}$ had previously been synthesized[14] by chlorination of $S_7$ and $S_8$ to give $S_7Cl_2$ and $S_8Cl_2$, respectively, which on treatment with $Cp_2TiS_5$ yielded $S_{11}$ and $S_{13}$. The application of this procedure to organic polysulfanes requires, however, that the SS bonds react much faster with the elemental chlorine than all other bonds in the molecule. In the examples presented in this work this condition is obviously met. It remains to be shown whether very large organic polysulfane molecules with more than 10 sulfur atoms in a chain or ring may be built up in this way also, e.g., by controlled chlorination of a decasulfane followed by the $S_5$ transfer reaction.

## EXPERIMENTAL

*Spectrometers*: Bruker WH 270 and WH 400 spectrometers (chem. shifts relative to TMS); Perkin-Elmer 580B infrared spectrophotometer with data processing terminal; ISA Raman spectrometer (double monochromator U 100 by Yvon Jobin) with GaAs photomultiplier, krypton ion laser (647.1 nm) and MAC 80 computer and terminal; double focusing mass spectrometer with inverse Nier-Johnson geometry and Kratos DS90 data terminal.

*HPLC equipment*: Perkin-Elmer liquid chromatograph series 10, Rheodyne loop injector (10 μl), Waters-Millipore Radial-Pak cartridge column (length 100 mm, inner diameter 8 mm) with octadecylsilane (particle size 10 μm) contained in a compression module, Waters-Millipore 990 diode-array detector (512 diodes, range 190–800 nm) with NEC APCIII computer and recorder.

*Chemicals*: The solvents methanol ($MgSO_4$), THF (Na), diethyl ether (KOH), hexane ($CaH_2$), $CS_2$, $CCl_4$, $CHCl_3$, $CH_2Cl_2$ (all $P_2O_5$) were distilled from the drying agents given in brackets. Chlorine was bubbled into $CCl_4$ at 0°C with weight control to prepare a solution of concentration 1.4 mmol ($Cl_2$)/mL. $Cp_2TiS_5$ was synthesized as described previously.[15]

*Tri-* (**2**) *and pentasulfane* (**3**) *of norbornane*: Following Bartlett and Ghosh's procedure[3] as closely as possible **2** and **3** were synthesized from $C_7H_{10}$ and $S_8$. **3** was recrystallized from *n*-pentane, and **2** was distilled twice in a vacuum. Yields based on 37.5 g norbornene: 13.7 g of **2**, and 4.5 g of **3**. HPLC analysis of the crude reaction product (ether extract) showed **2** and **3** present in a ca. 3:1 ratio with no other $C_7H_{10}S_n$ molecules detectable. Satisfactory elemental analyses were obtained for **2** and **3**, and the mass spectra showed the molecular ions. Crystals of **3** (m.p. 105°C) grown from pentane at 4°C were used for the structural analysis.[4] Anal. for **2**: calc. C, 44.2; H, 5.3; found C, 44.4; H, 5.4; for **3**: calc. C, 33.1; H, 3.9; found C, 33.6; H, 4.1%. Raman spectra of **2**: 1035 *w*, 998 *w*, 945 *w*, 920 *s*, 882 *m*, 869 *w*, 833 *vw*, 802 *vw*, 765 *vw*, 672 *s*, 619 *vw*, 513 *vs*, 479 *m*, 471 *m*, 413 *m*, 362 *s*, 305 *s*, 267 *s*, 219 *w*, 151 *m* ($cm^{-1}$), and of **3**: 1220 *vw*, 1173 *vw*, 1141 *vw*, 1116 *vw*, 1041 *vw*, 1003 *vw*, 951 *vw*, 922 *w*, 878 *vw*, 664 *w*, 622 *vw*, 512 *m*, 460 *s*, 438 *m*, 414 *m*, 351 *w*, 299 *w*, 248 *s*, 229 *w*, 219 *m*, 177 *s*, 162 *m*, 103 *m*, 95 *m*, 67 *vs* ($cm^{-1}$). $^1H$ NMR ($CDCl_3$) of **2**; expressed in $\delta$-scale ppm; H atoms marked as in Figure 1b: 3.64 ($d$, $J = 2$ Hz; $H_a$), 2.46 ($m$; $H_b$), 1.93 ($dm$, $J = 11$ Hz; $H_e$), 1.73 ($dm$, $J = 8$ Hz; $H_d$), 1.26 ($dm$, $J = 8$ Hz; $H_c$), 1.07 ($dm$, $J = 11$ Hz; $H_f$), and of **3**: 3.95 ($d$, $J = 2$ Hz; $H_a$), 2.44 ($m$; $H_b$), 1.65 ($m$, $H_d$ and $H_e$), 1.33 ($dm$, $J = 8$ Hz, $H_c$), 1.14 ($dm$, $J = 11$ Hz; $H_f$).

*Rel-(1R,2S,3R,4S)-bicyclo[2.2.1]heptane-2,3-bis(sulfenylchloride)* (**5**): 1.9 g of **2** and 10 mg $I_2$ were dissolved in 200 mL $CCl_4$ and with exclusion of air 18 mL chlorine solution (24.5 mmol $Cl_2$) were added dropwise at 0°C. Evaporation in a vacuum excess $Cl_2$, $CCl_4$, $SCl_2$, ICl, and $ICl_3$ and yielded 2.4 g of crude **5** as an orange oil; no spectra were recorded.

*Exo-3,4,5,6,7,8,9-heptathiatricyclo[9.2.1.0$^{2,10}$]tetradecane* (**7**): 1.9 g of **5** dissolved in 10 mL $CS_2$ were added dropwise to a solution of 1.69 g of **4** in 20 mL $CS_2$ at 20°C. After stirring for 1 h and filtering off the precipitated **9** the solution was overlayed with 5 mL *n*-hexane and stored at −78°C for 16 h resulting in a precipitate of 100 mg of **7** (yield 4% based on **5**); m.p. 80°C (dec.). Anal. calcd. for $C_7H_{10}S_7$: C, 26.4; H, 3.1; found C, 24.2; H, 3.0%. Mass spectrum (EI, 70 eV; 70°C): 318 (8; $M^+$), 254 (7; $M^+$-$S_2$), 224 (10; $S_7^+$), 222 (**8**; $M^+$-$S_3$), 190 (100; $M^+$-$S_4$), 158 (56; $M^+$-$S_5$), 126 (67; $M^+$-$S_6$), 97 (36; $HS_3^+$), 93 (70; $C_7H_9^+$), 77 (43; $C_6H_5^+$), 66 (96; $C_5H_6^+$).
Raman-spectrum (−100°C): 922 *w*, 670 *w*, 660 *w*, 514 *w*, 493 *w*, 489 *m*, 470 *s*, 445 *m*, 434 *w*, 417 *w*, 263 *w*, 205 *s*, 169 *w*, 149 *m*, 132 *w* ($cm^{-1}$). For NMR data see Table I.

*Rel-(1R,2S,3R,4S)-3-(chlordisulfanyl)bicyclo[2.2.1]-heptane-2-sulfenylchloride* (**6**): 10 mL chlorine solution (14.4 mmol $Cl_2$) were added dropwise to a solution of 1.3 g of **2** in 100 mL $CCl_4$. After stirring for 10 more min the mixture was brought to dryness in an oil pump vacuum resulting in 1.9 g of **6**. Anal. calcd. for $C_7H_{10}Cl_2S_3$: C, 32.3; H, 3.8; found: C, 31.3: H, 3.9%. Mass spectrum (EI, 70 eV; 25°C): 260 (2; $M^+$), 224 (12; $M^+$-HCl), 190 (53; $M^+$-$Cl_2$), 160 (27; $C_7H_9SCl^+$), 126 (9; $M^+$-$S_2Cl_2$), 93 (89; $C_7H_9^+$), 66 (100; $C_5H_6^+$).

*Exo-3,4,5,6,7,8,9,10-octathiatricyclo[10.2.1.0$^{2,11}$]pentadecane* (**8**): 1.9 g of **6** dissolved in 5 mL $CS_2$ were added dropwise to a mixture of 1.5 g of **4** and 15 mL $CS_2$. After cooling to −78°C the precipitated **9** was filtered off and the solution overlayed with 20 mL *n*-hexane whereupon 90 mg of **8** precipitated on standing at −78°C for 12 h (yield 4% based on $C_7H_{10}S_3$); m.p. 93°C.
Anal. calcd. for $C_7H_{10}Cl_2S_2$: C, 24.0; H, 2.9; found: C, 22.3; H, 2.4%. Mass spectrum (EI, 70 eV; 140°C): 320 (1; $S_{10}^+$), 256 (21; $S_8^+$), 254 (2; $M^+$-$S_3$), 224 (6; $S_7^+$), 192 (11; $S_6^+$), 190 (30; $M^+$-$S_5$), 160 (23; $S_5^+$), 126 (57; $M^+$-$S_7$), 93 (78; $C_7H_9^+$), 66 (100; $C_5H_6^+$). Raman spectrum (23°C): 1016 *vw*, 912 *vw*, 705 *vw*, 617 *vw*, 510 *w*, 499 *w*, 486 *w*, 454 *vs*, 443 *w*, 429 *w*, 414 *w*, 379 *vw*, 362 *w*, 326 *vw*, 286 *w*, 279 *w*, 263 *vw*, 244 *w*, 233 *m*, 207 *vw*, 187 *m*, 161 *s*, 145 *m*, 125 *m*, 112 *m*, 95 *vs*, 83 *sh*, 69 *sh* ($cm^{-1}$). For NMR data see Table IV.

*Chlorination of* **7** *and formation of* **11**: 2 mL chlorine solution (1.3 mmol $Cl_2$) were added dropwise to 508 mg of **3**, dissolved in 50 mL $CCl_4$, and samples of this solution were treated with $CS_2$ solutions of $Cp_2TiS_5$ at different stages of the chlorination reaction. Chromatograms were recorded after dilution (1:100) by $CH_2Cl_2$.

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