8056 *J. Org. Chem.* **1995**, *60*, 8056−8061

Synthesis of the Dicyclopentadiene Polysulfanes $C_{10}H_{12}S_n$ with n = 4−8 Using Titanocene Polysulfide Complexes as Sulfur-Transfer Reagents[†]

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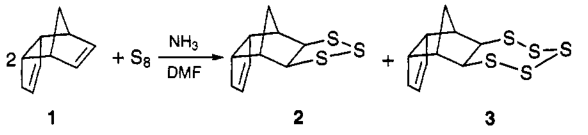
The dicyclopentadiene polysulfanes $C_{10}H_{12}S_n$ (n = 4−8) are prepared using the sulfur-transfer reagents Cp_2TiS_5 and $(Cp'_2TiCl)_2S_3$ ($Cp' = \eta^5$-$C_5H_4CH_3$) or S_2Cl_2 in combination with novel SCl derivatives of dicyclopentadiene of type $C_{10}H_{12}(S_nCl)(S_mCl)$ (n, m = 1, 2) or the dithiol of dicyclopentadiene, respectively. Dicyclopentadienedithiol $C_{10}H_{12}(SH)_2$ reacts with SO_2Cl_2 to give the bis(sulfenyl chloride) $C_{10}H_{12}(SCl)_2$ and with an excess of SCl_2 it yields the bis(chlorodisulfane) $C_{10}H_{12}(S_2Cl)_2$. The mixed sulfenyl chloride $C_{10}H_{12}(SCl)(S_2Cl)$ was obtained from $C_{10}H_{12}S_3$ by treatment with SO_2Cl_2. $C_{10}H_{12}(SH)_2$ and S_2Cl_2 give the novel $C_{10}H_{12}S_4$ while $C_{10}H_{12}S_5$ was obtained from $C_{10}H_{12}(SCl)_2$ and $(Cp'_2TiCl)_2S_3$. The latter complex reacts with $C_{10}H_{12}(SCl)(S_2Cl)$ to give $C_{10}H_{12}S_6$. The formation of $C_{10}H_{12}S_7$ from $C_{10}H_{12}(SCl)_2$ and Cp_2TiS_5 was demonstrated by HPLC. The reaction of $C_{10}H_{12}(SCl)(S_2Cl)$ with Cp_2TiS_5 afforded $C_{10}H_{12}S_8$. RP-HPLC is a suitable analytical method to determine the number of sulfur atoms n_S in $C_{10}H_{12}S_n$ species since the retention time systematically increases with increasing n_S. The ^{1}H NMR spectra of $C_{10}H_{12}S_n$ are different enough to allow the detection of these species in mixtures but in addition to the inductive effect of the varying number of sulfur atoms the conformation of the C_2S_n unit exercises an important influence on the chemical shift of the protons.

Introduction

On heating dicyclopentadiene (**1**) ($C_{10}H_{12}$) reacts with sulfur in the presence of a catalyst as NH_3 or Na_2S to give the trithiolane **2** and the pentathiepane **3** (eq 1).[1]



(1)

No other cyclic polysulfanes of **1** have so far been reported.[2] In connection with the chemistry of sulfur cement,[3] which is commercially produced from **1** and S_8 by heating to 140°C and which is believed to contain long-chain polysulfanes $-S_xRS_yRS_z$- ($R = C_{10}H_{12}$), we were interested in the synthesis of other cyclic polysulfanes of dicyclopentadiene, which obviously cannot be obtained by reaction 1. The properties of these polysulfanes, if known, may explain why such species are not formed in reaction 1. In addition we were interested in systematic studies of the ^{1}H NMR spectra of cyclic polysulfanes of the same organic skeleton with different polysulfane moieties hoping to find a relationship between the size of the polysulfane unit and the chemical shifts of the neighboring protons.

Titanocene pentasulfide, Cp_2TiS_5 (**4**), is known to react with SCl compounds with the transfer of sulfur. This capability has been used for the preparation of a large number of organic and inorganic, cyclic as well as chainlike polysulfanes.[4] Here we report the synthesis of three SCl derivatives of **1** and their reactions with **4** and with $(Cp'_2TiCl)_2S_3$ (**5**, $Cp' = \eta^5$-$C_5H_4CH_3$)[5] to give the new polysulfanes $C_{10}H_{12}S_n$ (n = 5−8), while the tetrasulfane of **1** was obtained from the dithiol of **1** by reaction with S_2Cl_2.

Results

Chlorosulfane Derivatives of Dicyclopentadiene, $C_{10}H_{12}(S_mCl)(S_nCl)$ (n, m = 1,2). The trithiolane **2** was used as a starting material for the synthesis of SCl derivatives of dicyclopentadiene of type $C_{10}H_{12}(S_mCl)(S_nCl)$ (n, m = 1, 2) (Scheme 1).

$C_{10}H_{12}(SCl)(S_2Cl)$. Chlorination of **2** with 1 equiv of sulfuryl chloride in diethyl ether resulted in a quantitative yield of $C_{10}H_{12}(SCl)(S_2Cl)$ (**6**). The yellow, moisture-sensitive solid obtained after removing the solvent was recrystallized from CH_2Cl_2. Treatment of **6** with **4** resulted in the formation of $C_{10}H_{12}S_8$ (**10**) and Cp_2TiCl_2 (see below), thus confirming the connectivity of **6**. The

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[†] Sulfur Compounds, Part 190; for Part 189, see: Steudel, R. *Angew. Chem.* **1995**, *107*, 1433; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1313.

[®] Abstract published in *Advance ACS Abstracts*, November 1, 1995.

(1) (a) Bartlett, P. D.; Ghosh, T. *J. Org. Chem.* **1987**, *52*, 4937. (b) Emsley, J.; Griffiths, D. W.; Jayne, G. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 228. (c) Hofmann, J.; Dimmig, T.; Jäger, G. *Z. Chemie* **1990**, *30*, 371. (d) DD-Patent: 263.770, 1989; Hoffmann, J.; Fischer, R.; Jäger, G.; Zimmermann, V.; Kräuter, D.; Öhler, R.; Knopel, E. *Chem. Abstr.* **1989**, *111*, 134207s. (e) DD-Patent: 263.787, 1989; Hoffmann, J.; Fischer, R.; Jäger, G.; Zimmermann, V.; Öhler, R.; Knopel, E. *Chem. Abstr.* **1989**, *111*, 137360x. (f) DD-Patent: 263.788, 1989; Hoffmann, J.; Fischer, R.; Jäger, G.; Zimmermann, V.; Öhler, R.; Knopel, E. *Chem. Abstr.* **1989**, *111*, 81188c. (g) DD-Patent: 270.317, 1989; Hoffmann, J.; Fischer, R.; Jäger, G.; Zimmerman, V.; Kräuter, D.; Öhler, R.; Knopel, E. *Chem. Abstr.* **1989**, *112*, 80816q.

(2) Steudel, R.; Kustos, M. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley, J.; Sussex, **1994**; Vol. 7, 4009ff.

(3) (a) Blight, L.; Currell, B. R.; Nash, B. J.; Scott, R. A. M.; Stillo, C. In *Organic Sulfur Chemistry: Biochemical Aspects*; Oae, S., Ed.; CRC Press: Tokyo, 1992; Chapter 2. (b) Blight, L.; Currell, B. R.; Nash, B. J., Scott, R. A. M.; Stillo, C. *Brit. Polym. J.* **1980**, 5. (c) Bordoloi, B. K.; Pearce, E. M.; Blight, L.; Currell, B. R.; Merrall, R.; Scott, R. A. M.; Stillo, C. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 383.

(4) (a) Steudel, R. In *The Chemistry of Inorganic Ring Systems - Studies in Inorganic Chemistry*; Steudel, R., Ed.; Elsevier Science Publishers B.V.: Amsterdam, **1992**; Vol. 14, Chapter 13 and references cited therein. (b) Steudel, R.; Kustos, M.; Pridöhl, M.; Westphal, U. *Phosphorus Sulfur Silicon* **1994**, *93–94*, 61.

(5) Prenzel, A. Doctoral Dissertation, Technische Universität Berlin, 1992.

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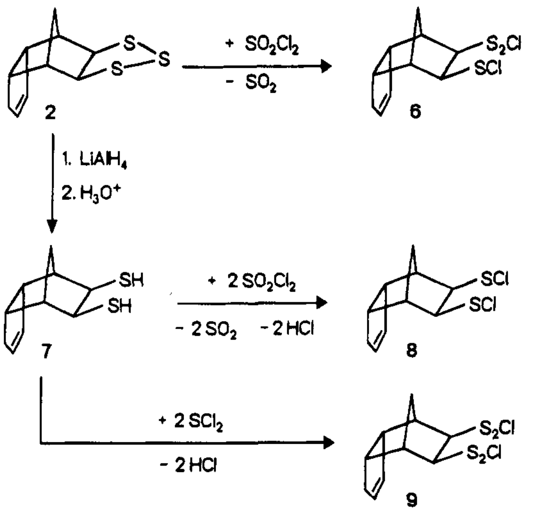
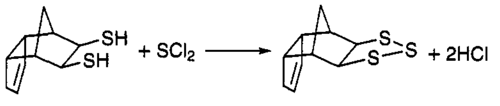
Scheme 1

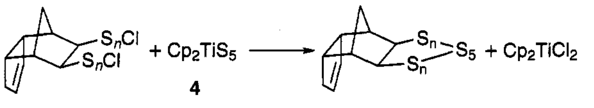


vibrational spectra of **6** are in comparison with the spectra of S_nCl_2 (n = 1, 2)[6] and of $Ph_3CS_nCl_2$ (n = 1−3)[7] in agreement with the presence of both an SCl and an S_2Cl moiety. The three IR absorptions and three Raman signals observed between 400 and 600 cm^{-1} are assigned as follows: ν_{SCl} (S_2Cl) 445 cm^{-1}; ν_{SCl} (SCl) 476 cm^{-1}; ν_{SS} (S_2Cl) 517 cm^{-1}.

$C_{10}H_{12}(S_nCl)_2$. The two symmetrical chlorosulfanes $C_{10}H_{12}(S_nCl)_2$ (n = 1, **8**; n = 2, **9**) were obtained from the dithiol **7**[1a] by condensation reactions with SO_2Cl_2 (n = 1) or SCl_2 (n = 2), respectively. To synthesize the bis(chlorodisulfane) **9** a low reaction temperature (−78 °C) and an excess of SCl_2 was necessary to suppress the formation of the trithiolane **2** (eq 2). The bis(chlorosulfanes) **8** and **9** are moisture-sensitive yellow products; **8** is a solid but **9** is an oil at 20 °C. Although the microanalyses were not satisfactory since the solvents could not be removed completely in both cases, the compounds were identified by their spectra and in particular by their reactivity toward **4**: in agreement with eq 3 only two products were detected by RP-HPLC in each case (Cp_2TiCl_2 and **11** or **12**, respectively). This shows that **8** and **9** are not contaminated by other SCl compounds. The Raman spectra of **8** and **9** support the proposed structures. The S−Cl stretching modes of $C_{10}H_{12}(SCl)_2$ (**8**) are observed as a single broad signal at 481 cm^{-1}. The most intense Raman signal of **9** appears at $\tilde{\nu}$ = 445 cm^{-1} and is assigned to ν_{SCl}; the ν_{SS} mode is detected at 527 cm^{-1}. These assignments are in accord with those given above for **6** and with the spectra of SCl_2 and S_2Cl_2.[8] The EI mass spectrum of **8** (sample temperature 90 °C) shows the molecular ion at 266 m/z.



7 2 (2)



4 (3)

n = 1: **8**
n = 2: **9**

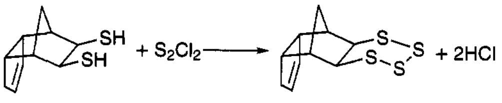
n = 1: **11**
n = 2: **12**

Table 1. EI Mass Spectra (70 eV) of $C_{10}H_{12}S_4$ (T = 260 °C) and $C_{10}H_{12}S_8$ (T = 140 °C)

	rel intensity		
m/z	$C_{10}H_{12}S_4$	$C_{10}H_{12}S_8$	assignment
324	0	1.5	$C_{10}H_{12}S_6^+$
292	6	5.5	$C_{10}H_{12}S_5^+$
256	0	32	S_8^+
228	70	50	$C_{10}H_{12}S_3^+$
192	0	18	S_6^+
163	37	35	$C_{10}H_{11}S^+$
160	0	31	S_5^+
131	100	80	$C_{10}H_{11}^+$
129	20	29	$C_{10}H_9^+$
128	0	36	S_4^+
66	58	100	$C_5H_6^+$

Dicyclopentadiene Polysulfanes $C_{10}H_{12}S_n$ (n = 3−8). $C_{10}H_{12}S_3$. Compound **2** was synthesized as described previously.[1] The molecular structure has been elucidated by X-ray crystallography.[9] The results demonstrate for the first time that the sulfur atoms are connected to the norbornane skeleton in *exo* positions and that the five-membered ring containing the trisulfane moiety exhibits an envelope conformation.

$C_{10}H_{12}S_4$. By applying the dilution principle, the tetrathiane $C_{10}H_{12}S_4$ (**13**) was prepared by adding solutions of **7** and S_2Cl_2, respectively, in diethyl ether to a large volume of diethyl ether at 0 °C (eq 4). The product **13** was obtained from the bright yellow solution by reducing the solvent volume to half of its original value at 0 °C. Precipitation of $C_{10}H_{12}S_4$ was achieved by cooling the solution to −78 °C.



7 13 (4)

The microanalysis is satisfactory for the composition $C_{10}H_{12}S_4$, and the RP-HPLC consists of only one signal. This not only proves the purity of the sample but also the identity since the retention time is between those of **2** and **3** (see below). The retention time of a conceivable product like a dimeric or oligomeric species $(C_{10}H_{12}S_4)_n$ from reaction **4** would be much longer since t_R depends on the size of a molecule. The Raman spectrum of **13** shows the S−S stretching modes at 356, 495, and 532 cm^{-1}. The EI mass spectrum (sample temperature 260 °C) does not show a peak for the molecular ion, but $C_{10}H_{12}S_5^+$ and $C_{10}H_{12}S_3^+$ were detected instead. By taking into account that the tetrathiane decomposes at ambient temperature in the solid state and in solution to the corresponding trithiolane and the pentathiepane (eq 5), the EI mass spectrum is assigned to the ions originating from the decomposition products of $C_{10}H_{12}S_4$ (see Table 1).

$$2C_{10}H_{12}S_4 \rightarrow C_{10}H_{12}S_3 + C_{10}H_{12}S_5 \qquad (5)$$

$C_{10}H_{12}S_5$. Although the pentathiepane **3** is formed along with $C_{10}H_{12}S_3$ (**2**) by the reaction of dicyclopenta-

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[6] (a) Stammreich, H.; Forneris, R.; Sone, K. *J. Chem. Phys.* **1955**, *23*, 972. (b) Frankiss, S. G. *J. Mol. Struct.* **1968**, *2*, 271.

[7] Albertsen, J. Doctoral Dissertation, Technische Universität Berlin, 1993.

[8] Steudel, R.; Jensen, D.; Plinke, B. *Z. Naturforsch., Part B*, **1987**, *42*, 163 and references cited therein.

[9] The atomic coordinates of **2** have been deposited with the Cambridge Crystallographic Data Centre. They can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

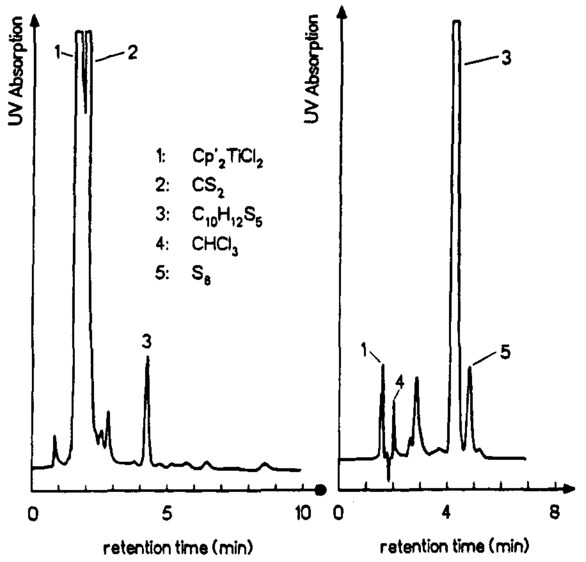

Figure 1. HPLC traces of the reaction mixture of $C_{10}H_{12}(SCl)_2$ with $(Cp'_2TiCl)_2S_3$ (left) and of the desired product $C_{10}H_{12}S_5$ after purification by preparative TLC (right) of the desired product $C_{10}H_{12}S_5$ after purification by preparative TLC (right).

diene with sulfur (eq 1), the preparation of pure **3** has failed until now. Therefore, the product has only been characterized as the main component (85%) of a mixture with the trisulfane.[1a]

Using $(Cp'_2TiCl)_2S_3$ as a sulfur transfer reagent and **8** as the organosulfenyl chloride we succeeded in generating $C_{10}H_{12}S_5$ without any $C_{10}H_{12}S_3$ as byproduct (eq 6). HPLC analysis of the reaction mixture showed the pentathiepane **3** along with Cp'_2TiCl_2 as well as two unknown products in low concentrations. The mixture was separated nearly quantitatively by preparative TLC on reversed-phase material using methanol as an eluent (see Figure 1). The use of silica gel for preparative TLC resulted in a partial decomposition of $C_{10}H_{12}S_5$ to the trithiolane **2** and elemental sulfur (eq 7), indicating that the two polysulfanes cannot be separated by this method as has been tried previously.[1a]

$$C_{10}H_{12}(SCl)_2\ (\mathbf{8}) + (Cp'_2TiCl)_2(\mu\text{-}S_3)\ (\mathbf{5}) \rightarrow C_{10}H_{12}S_5\ (\mathbf{3}) + 2Cp'_2TiCl_2 \qquad (6)$$

$$C_{10}H_{12}S_5 \xrightarrow{[SiO_2]} C_{10}H_{12}S_3 + {}^1\!/_4S_8 \qquad (7)$$

$C_{10}H_{12}S_6$. The reaction of equimolar amounts of $(Cp'_2TiCl)_2S_3$ (**5**) with **6** in carbon disulfide at ambient temperature yields quantitatively $C_{10}H_{12}S_6$ and Cp'_2TiCl_2 (eq 8). The solution was filtered through a short column of silica gel which absorbs Cp'_2TiCl_2. After removal of the solvent, $C_{10}H_{12}S_6$ (**14**) was obtained as a yellow solid. Although traces of other $C_{10}H_{12}S_n$ molecules were detected by RP-HPLC (see Figure 2) the microanalysis of **14** was satisfactory.

$$C_{10}H_{12}(SCl)(S_2Cl)\ (\mathbf{6}) + (Cp'_2TiCl)_2(\mu\text{-}S_3)\ (\mathbf{5}) \rightarrow C_{10}H_{12}S_6\ (\mathbf{14}) + 2Cp'_2TiCl_2 \qquad (8)$$

By reversed-phase liquid chromatography it is possible to determine the number of sulfur atoms of organic polysulfanes, since the HPLC retention times (t_R) systematically depend on the number of sulfur atoms (n_S). A linear correlation is obtained when the logarithm of the capacity factor k' [$k' = (t_R - t_0)/t_R$; t_0 = dead time] is plotted versus n_S.[10] Retention indices (RS), which normalize the retention times relative to those of the cyclic S_n molecules with n = 6, 8, 9, and 10, are independent of the flow and of the apparatus but depend on the eluent.[10a] Demonstrating the linear correlation between RS and n_S for $C_{10}H_{12}S_n$ species applying two different eluents (see Figure 3 and Table 2) and using the trithiolane and the pentathiepane for calibration, the product obtained in eq 8 was identified as the hexasulfane **14**.

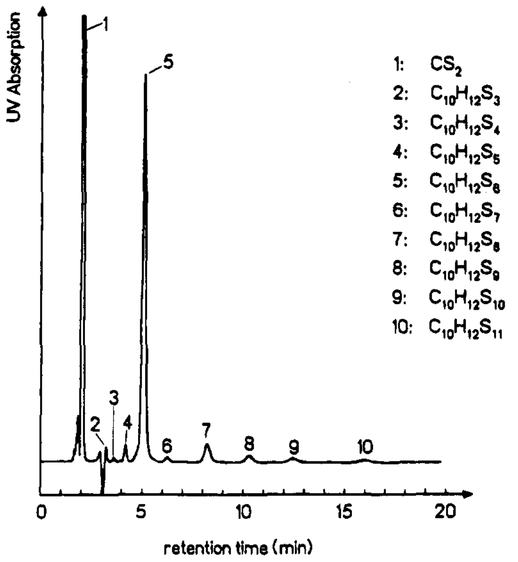

Figure 2. HPLC analysis of $C_{10}H_{12}S_6$ dissolved in CS_2.

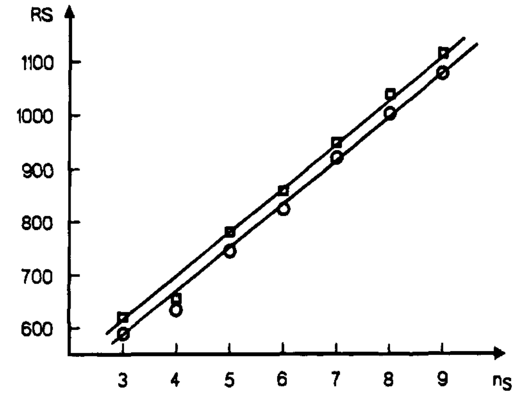

Figure 3. Retention behavior of dicyclopentadiene polysulfanes $C_{10}H_{12}S_n$. The retention index RS versus the number of sulfur atoms n_S for two eluents is plotted: (○) methanol; (□) methanol/water, 95/5.

The EI mass spectrum (sample temperature 130 °C) of **14** does not show the molecular ion but is characterized by fragments resulting from M^+ by the loss of S_n units. This result is typical for sulfur-rich organic polysulfanes.[11] The ^1H NMR spectrum of **14** is similar to those of **2** and **3**; however, the chemical shifts of some protons are different (see below, discussion of ^1H NMR spectra of all investigated polysulfanes).

$C_{10}H_{12}S_7$. As mentioned above, the reaction of $C_{10}H_{12}(SCl)_2$ with Cp_2TiS_5 yields two products, Cp_2TiCl_2

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[10] (a) Steudel, R.; Strauss, E.-M. *Z. Naturforsch., Part B*, **1983**, *38*, 719. (b) Steudel, R.; Kustos, M. *Phosphorus Sulfur Silicon* **1991**, *62*, 127.

[11] Steudel, R.; Förster, S.; Albertsen, J. *Chem. Ber.* **1991**, *124*, 2357.

Table 2. Retention Data of Dicyclopentadiene Polysulfanes $C_{10}H_{12}S_n$[a]

	RS	
ns	eluent 1	eluent 2
3	589	621
4	634	656
5	745	780
6	823	857
7	920	953
8	1003	1038
9	1078	1115

[a] RS: retention indices related to those of S_n molecules (n = 6, 8, 9, 10); n_S: number of sulfur atoms; eluent 1 is methanol; eluent 2 is methanol/water, 95/5.

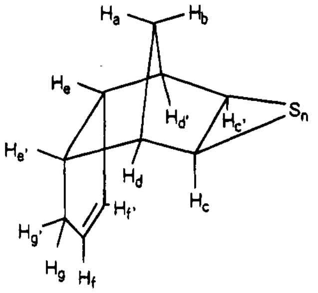

Figure 4. Labeling of the hydrogen atoms in $C_{10}H_{12}S_n$ molecules.

and the novel heptathionane **11**. Attempts to obtain pure **11** from these solutions were not successful, since even at low temperatures the product decomposes rapidly both in the solid state and in solution to give mixtures of $C_{10}H_{12}S_n$ molecules and elemental sulfur. The following reactions may take place (eqs 9a–e):

$$2C_{10}H_{12}S_7 \rightleftharpoons C_{10}H_{12}S_6 + C_{10}H_{12}S_8 \qquad (9a)$$

$$2C_{10}H_{12}S_8 \rightleftharpoons C_{10}H_{12}S_7 + C_{10}H_{12}S_9 \qquad (9b)$$

$$2C_{10}H_{12}S_9 \rightleftharpoons C_{10}H_{12}S_3 + S_6 \qquad (9c)$$

$$C_{10}H_{12}S_7 + S_6 \rightleftharpoons C_{10}H_{12}S_5 + S_8 \qquad (9d)$$

$$S_6 + S_8 \rightleftharpoons 2S_7 \qquad (9e)$$

$C_{10}H_{12}S_8$. $C_{10}H_{12}S_8$ (**10**) was synthesized from $C_{10}H_{12}(S_2Cl)(SCl)$ (**6**) and Cp_2TiS_5 (eq 10). The reaction was carried

$$C_{10}H_{12}(SCl)(S_2Cl)\ (\mathbf{6}) + Cp_2TiS_5\ (\mathbf{4}) \rightarrow C_{10}H_{12}S_8\ (\mathbf{10}) + Cp_2TiCl_2 \qquad (10)$$

out in CS_2 at 20 °C. To separate the two products, the resulting mixture was stored at −78 °C for 24 h affording a precipitate of Cp_2TiCl_2 which was filtered off. The octathiecane **10** was obtained as a colorless solid after evaporation of the solvent and washing the remaining rosy residue with chloroform to remove traces of Cp_2TiCl_2.

The novel octathiecane **10** was identified by microanalysis and its retention index RS, which fits the linear correlation between RS and the number of sulfur atoms n_S (see Figure 4). The EI mass spectrum (sample temperature 140 °C) is characterized by the loss of S_n units and does not show the molecular ion (see Table 1). In the solid state **10** decomposes mainly to sulfur and **2** along with some **3**.

^{1}H NMR Spectra of $C_{10}H_{12}S_n$ (n = 3–8). The proton NMR spectra of the described polysulfanes of dicyclopentadiene show remarkable similarities which indicate identical *exo* positions of the sulfur atoms with respect to the norbornane group for all compounds. Consequently, the assignment for the trisulfane[1] will be used as a guide to assign the spectra of the other polysulfanes (see Table 3). The ^{1}H NMR spectra show between 9 and 11 lines. This indicates that the molecules have no symmetry and that some of the 12 expected peaks overlap.

The protons $H_c/H_{c'}$ (see Figure 4) couple with each other (vicinal coupling: J = 7 Hz) and with H_a (w-coupling: J = 1.5 Hz). The corresponding signal appears as a sharp doublet of doublets. In contrast, the resonances of the protons H_a and H_b result in broad doublets indicating that the geminal coupling (J = 11 Hz) is accompanied by vicinal couplings to the protons $H_d/H_{d'}$. The resonances of the protons $H_d/H_{d'}$ are observed as broad multiplets due to couplings with H_a as well as H_b and $H_e/H_{e'}$. The olefinic protons occur at about 5.7 ppm as expected. Of the remaining signals the one at lowest magnetic field is assigned to H_e taking the influence of the neighboring double bond and the different resonance behavior of methylene and methine protons into account.

Only the chemical shifts of the protons neighboring the sulfur atoms are significantly different for the five polysulfanes investigated and among these it is only the shift of H_b which seems to depend on the number of sulfur atoms in the ring. In analogy to the findings with linear polysulfanes RS_nR[12] (e.g. R = H,[13] $C_{14}H_{19}O_9$[14]) we expected that the more sulfur atoms, the lower the magnetic field at which the peak would be observed. By way of contrast, the chemical shift of H_b decreases with increasing number of sulfur atoms. The conformation of the C_2S_n ring causing an anisotropic effect for proton H_b, seems to be more important than the inductive effect related to the number of sulfur atoms.

Summary

The dicyclopentadiene trisulfane $C_{10}H_{12}S_3$ has been shown to serve as a precursor for the preparation of the homologous compounds $C_{10}H_{12}S_n$ with n = 4–8. First the trisulfane was functionalized to give either the dithiol $C_{10}H_{12}(SH)_2$ or the mixed sulfenyl chloride $C_{10}H_{12}(SCl)(S_2Cl)$. From the dithiol the symmetrical sulfenyl chlorides $C_{10}H_{12}(SCl)_2$ and $C_{10}H_{12}(S_2Cl)_2$ were obtained. These SCl derivatives react under mild conditions with the sulfur-transfer reagents Cp_2TiS_5 and $(Cp'_2TiCl)_2S_3$ to give the polysulfanes $C_{10}H_{12}S_n$ with n = 5–8 while the tetrasulfane was obtained from the dithiol by reaction with S_2Cl_2. The latter compounds are thermally labile and tend to decompose to mixtures of $C_{10}H_{12}S_3$, $C_{10}H_{12}S_5$, and S_8; therefore, they are not observed under the conditions as applied in reaction 1. Since the HPLC retention times systematically depend on the number of sulfer atoms n_S this analytical method allows their determination. In addition, the ^{1}H NMR spectra of $C_{10}H_{12}S_n$ molecules are specific enough to be used as a probe of these species in mixtures.

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[12] Cardone, M. J. In Karchmer, J. H., Ed; *The Analytical Chemistry of Sulfur and its Compounds, Part II*; Wiley & Sons: New York, 1972; p 198ff and references cited therein.

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Table 3. ^{1}H NMR spectra of $C_{10}H_{12}S_n$ and Assignment to the Atoms as Labeled in Figure 5[a]

assignment	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 8$
$H_{f'}/H_f$	5.73, 5.61	5.75, 5.66	5.80, 5.62	5.72, 5.64	5.75, 5.60
H_c/H_c'	3.72, 3.68	3.70	3.98, 3.89	3.42, 3.30	3.80, 3.50
H_e	3.27	3.26	3.15	3.15	3.15
$H_{e'}$	2.70	2.76	2.71	2.62	2.70
$H_{d'}$	2.60			2.72	
$H_d/H_g/H_{g'}$	2.35	2.58, 2.34	2.30	2.50, 2.32	2.40
H_b	2.10	1.94	1.80	1.71	1.85
H_a	1.30	1.51	1.38	1.54	30

[a] δ is ppm; samples dissolved in $CDCl_3$; frequency 200 MHz ($n = 6$), 270 MHz ($n = 4$); 400 MHz ($n = 3, 5, 8$).

Experimental Section

Spectrometers. ^{1}H NMR spectra were obtained on 200, 270 and 400 MHz spectrometers. The samples were measured in $CDCl_3$, which was used as internal reference. The Raman spectra were measured with a GaAs photomultiplier, krypton ion laser (647.1 nm). Measurement conditions and sample preparation are noted separately. The mass spectra were obtained in the EI mode with an ionizing energy of 70 eV.

Chromatography. HPLC was done on a Waters-Millipore Radial-Pak cartridge column (length, 100 mm; inner diameter, 8 mm) with octadecylsilane (particle size, 10 μm), UV detector (λ = 254 nm). Methanol was used as an eluent unless otherwise noted. Preparative TLC analyses were performed on 20 × 20 glass plates coated with octadecylsilane (RP-18 F245S) by Merck. Silica gel was received from Merck ($60F_{254}$).

Chemicals. The solvents Et_2O (Na), CH_3OBu^t (Na), CS_2, $CHCl_3$, CH_2Cl_2, *n*-pentane (all P_4O_{10}) were distilled from the drying agents given in parentheses. SCl_2 and S_2Cl_2 were purified by standard methods.[15] Cp_2TiS_5 (**4**),[16] $(Cp'_2TiCl)_2S_3$ (**5**),[5] $C_{10}H_{12}S_3$ (**2**),[1] and $C_{10}H_{12}(SH)_2$ (**7**)[1a] were prepared as reported. Other solvents and chemicals were used as obtained without purification.

Tricyclo[5.2.1.0^{2,6}]dec-3-ene-8,9-disulfenyl Chloride (8). With exclusion of air and moisture 1 mL (12 mmol) of SO_2Cl_2 in 10 mL of CS_2 was added dropwise to a solution of 990 mg (5 mmol) of **7** in 50 mL of CS_2 at 0 °C. The solvent was removed from the yellow reaction mixture under reduced pressure: 1.34 g (5 mmol) of **8** remained as deep yellow solid; MS (90 °C) *m/z* (relative intensity) 266 (M^+; 3), 231 (3), 228 (7), 196 (5), 66 (100); Raman spectrum (20 °C, in CS_2) $\tilde{\nu}$ 459 (sh), 481 (s), 656 (vs), 703 (m), 796 (vs), 804 (s) cm^{-1}.

9-(Chlorodisulfanyl)tricyclo[5.2.1.0^{2,6}]dec-3-ene-8-sulfenyl Chloride (6). With exclusion of air and moisture a mixture of 4.56 g (20 mmol) of **2**, dissolved in 60 mL of Et_2O, and 1.6 mL (20 mmol) of SO_2Cl_2 was stirred for 2 h. The solvent was removed under reduced pressure until the product started to precipitate. The suspension was stored for 72 h at 4 °C and filtered. The remaining product **6** was recrystallized from CH_2Cl_2 by overlaying with *n*-pentane. On storage of the solution for 24 h at 4 °C, 4.04 g (13.5 mmol) of **6** precipitated: MS (350 °C) *m/z* (relative intensity) 262 (M^+ − Cl; 0.5), 228 (3), 197 (0.3), 163 (2.3), 131 (5.5), 129 (3), 115 (1), 98 (6), 97 (4), 91 (3), 66 (21), 36 (100); IR (KBr) $\tilde{\nu}$ 342 (w) 445 (s), 480 (s), 520 (w) cm^{-1}; Raman spectrum (20 °C) $\tilde{\nu}$ 271 (w), 347 (s), 365 (s), 445 (vs), 476 (vs), 517 (s) cm^{-1}. Anal. Calcd. for $C_{10}H_{12}S_3Cl_2$: C, 40.1; H, 4.0. Found: C, 39.8; H, 4.1.

8,9-Bis(chlorodisulfanyl)tricyclo[5.2.1.0^{2,6}]dec-3-ene (9). With exclusion of air and moisture 1.07 g (5.4 mmol) of **7** in 50 mL of CH_3OBu^t were added dropwise within 80 min to 0.8 mL (12.6 mmol) of dichlorosulfane in 40 mL CH_3OBu^t at −78 °C. Within 1 h the temperature was allowed to rise to 20 °C and the solvent was removed. Compound **9** remained as a yellow oil (670 mg): Raman spectrum (20 °C) $\tilde{\nu}$ 270 (m), 445 (s), 527 (w) cm^{-1}.

***exo*-4,5,6,7-Tetrathiatetracyclo[8.3.01^{2,9}.0^{3,8}]tetradec-11-ene (13).** Within 90 min solutions of 400 mg (2 mmol) of **7** in 100 mL of ether and 0.16 mL (2 mmol) dichlorodisulfane in 100 mL of ether were added dropwise and simultaneously to 150 mL of ether at 0 °C. After the solvent volume, at 0 °C, was reduced to half of its original value, the product precipitated from the bright yellow solution. The suspension was stored for 18 h at −78 °C and 52 mg (0.2 mmol) of **13** was filtered off: mp 113−120 °C dec; MS (260 °C) *m/z* (relative intensity) 292 (6), 228 (70), 163 (37), 131 (100), 129 (20), 66 (58); ^{1}H NMR (270 MHz, in $CDCl_3$) δ 5.75 (1 H), 5.66 (1 H), 3.70 (2 H), 3.26 (1 H), 2.76 (2 H), 2.58 (1 H), 2.34 (2 H), 1.94 (d, ^2J = 9 Hz, 1 H), 1.51 (d, ^2J = 9 Hz, 1 H); due to the low solubility of $C_{10}H_{12}S_4$ in chloroform the signals were broad and the couplings could not be observed for all protons; Raman spectrum (−110 °C) $\tilde{\nu}$ 356 (s), 495 (s), 532 (s) cm^{-1}. Anal. Calcd. for $C_{10}H_{12}S_4$: C, 46.2; H, 4.6. Found: C, 45.2; H, 4.5.

***exo*-4,5,6,7,8-Pentathiatetracyclo[9.3.0]^{2,10}.0^{3,9}]pentadec-12-ene (3).** To a solution of 28.9 mg (0.05 mmol) of **5** in 20 mL of CS_2 was added 13.4 mg (0.05 mmol) of **8** in 1 mL CS_2. The color of the reaction mixture changed from green to red, indicating complete reaction. To remove Cp'_2TiCl_2, 1 g of silica gel was added. After 10 min the mixture was filtered, and the volume of the solvent was reduced to a fifth. The solution was subjected to preparative TLC on reversed-phase (C18) material using methanol as an eluent. The main fraction (2.7 mg) was found to be **3** of 85% purity.

***exo*-4,5,6,7,8,9-Hexathiatetracyclo[10.3.0.1^{2,11}.0^{3,10}]-hexadec-13-ene (14).** **6** (300 mg, 1 mmol) in 10 mL CS_2 was added to a solution of 579 mg (1 mmol) of **5** in 100 mL of CS_2. The color of the reaction mixture changed from green to red, indicating complete reaction. The solution was filtered through a column with silica gel which absorbs Cp'_2TiCl_2. To increase the yield of **14**, the silica gel was washed with CS_2 as long as the filtrate was yellow: Yield 180 mg (0.55 mmol) of **14** from the filtrate after removing the solvent under reduced pressure: MS (130 °C) *m/z* (relative intensity) 292 (9), 256 (17), 228 (63), 196 (5), 192 (10), 163 (42), 160 (18), 131 (100), 128 (32), 98 (58), 91 (47), 77 (12), 66 (95); ^{1}H NMR (200 MHz, in $CDCl_3$) δ 5.72 (m, 1 H), 5.64 (m, 1 H), 3.42 (dd, ^3J = 7.5 Hz, ^4J = 2.5 Hz, 1 H), 3.30 (dd, ^3J = 7.5 Hz, ^4J = 2.5 Hz, 1 H), 3.15 [dddd, ^3J = 9 Hz (2 times), ^3J = 4 Hz (2 times), 1 H; the sum of the couplings results in seven nearly equidistant lines with intensities 1:2:3:4:3:2:1.], 2.72 (brd, ^3J = 5 Hz, 1 H), 2.62 [dddd, ^3J = 9 Hz (2 times), ^3J = 4 Hz (2 times); 1 H, the sum of the couplings results in seven nearly equidistant lines with intensities 1:2:3:4:3:2:1.], 2.50 (brd, ^3J = 5 Hz, 1 H), 2.38−2.27 (m, 2 H), 1.71 (brd, ^2J = 10 Hz, 1 H), 1.54 (brd, ^2J = 10 Hz, 1 H). Anal. calcd. for $C_{10}H_{12}S_6$: C, 37.0; H, 3.7. Found: C, 38.0; H, 3.7.

Reaction of Tricyclo[5.2.1.0^{2,6}]dec-3-ene-8,9-disulfenyl Chloride (8) with Titanocene Pentasulfide (4). A solution of 1.69 g (5 mmol) of **8** in 25 mL of CS_2 was added slowly to a solution of 1.34 g (5 mmol) of **4** in 125 mL of CS_2 at 0 °C. The reaction mixture cleared up to an orange color. *exo*-4,5,6,7,8,9,-10-Heptathiatetracyclo[11.3.0.1^{2,12}.0^{3,11}]heptadec-14-ene (**11**) was identified by RP-HPLC, but decomposed too rapidly into sulfur and other $C_{10}H_{12}S_n$ molecules to be isolated.

***exo*-4,5,6,7,8,9,10,11-Octathiatetracyclo[12.3.0.1^{2,13}.0^{3,12}]-octadec-15-ene (10).** A solution of 540 mg (1.8 mmol) of **6** in 10 mL of CS_2 was added slowly to a solution of 600 mg (1.8 mmol) of **4** in 40 mL of CS_2. After 20 min the reaction mixture cleared up to an orange color. The volume of the solvent was reduced to 20 mL and the solution stored at −78 °C for 24 h.

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Cp_2TiCl_2 was filtered off: yield 480 mg (1.24 mmol) of **10** as colorless solid after removal of the solvent and washing the remaining rosy residue with chloroform, mp 180 °C dec; ^1H NMR (400 MHz, in $CDCl_3$) δ 5.75 (1 H), 5.60 (1 H), 3.80 (1 H), 3.50 (1 H), 3.15 (1 H), 2.70 (2 H), 2.40 (3 H), 1.85 (1 H), 1.30 (1 H); due to the low solubility of $C_{10}H_{12}S_8$ in chloroform the signals were broad and the couplings could not be determined accurately; MS (140 °C) m/z (relative intensity) 324 (1.5), 292 (5.5), 256 (32), 228 (50), 192 (18), 163 (35), 160 (31), 131 (80), 129 (34), 128 (36), 66 (100). Anal. Calcd for $C_{10}H_{12}S_8$: C, 30.9; H, 3.1. Found: C, 30.3; H 3.0.

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